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THE CHEMICAL NEWS, JULY 26, 1912

THE  
CHEMICAL NEWS

AND  
JOURNAL OF PHYSICAL SCIENCE.

WITH WHICH IS INCORPORATED THE "CHEMICAL GAZETTE."

*A Journal of Practical Chemistry*

IN ALL ITS APPLICATIONS TO

PHARMACY, ARTS, AND MANUFACTURES.

EDITED BY

SIR WILLIAM CROOKES, O.M., D.Sc., F.R.S., &c.

VOLUME CV.—1912.

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# THE CHEMICAL NEWS.

VOLUME CV.

EDITED BY SIR WILLIAM CROOKES, O.M., D.Sc., F.R.S., &c.

No. 2719.—JANUARY 5, 1912.

## ON THE SPECTRUM OF BORON.\*

By Sir WILLIAM CROOKES, O.M., For. Sec. R.S.

THE first published account I can find of the ultra-violet spectrum of boron is by W. N. Hartley in 1883 (*Proc. Roy. Soc.*, vol. xxxv., p. 301; and *CHEMICAL NEWS*, vol. xlviii., p. 1), who obtained it by submitting saturated solutions of boric acid and of borax to the action of an induction spark. He describes it as consisting of three strong lines, of wave-lengths 3450·3, 2497·0, and 2496·2.

Rowland in his "New Table of Standard Wave-lengths" (*Phil. Mag.*, 1893, xxxvi., p. 49) gives the wave-lengths of two boron lines as 2497·821 and 2496·867. He does not mention a third line.

In 1893 J. M. Eder and E. Valenta (*Acad. der Wissensch. in Wien*) gave a list of seventeen lines in the ultra-violet spectrum of boron, their wave-lengths being:—

|         |         |
|---------|---------|
| 3957·9  | 2496·8† |
| 3941·7  | 2388·5  |
| 3829·3  | 2267·0  |
| 3824·5  | 2266·4  |
| 3451·3† | 2088·8  |
| 3246·9  | 2088·4  |
| 2689·0  | 2066·2  |
| 2686·2  | 2064·6  |
| 2497·7† |         |

In 1897 F. Exner and E. Haschek (*Akad. der Wissensch. in Wien*, Denkschriften, vol. lx., July, 1897, vol. cvi.) recorded eight lines in the ultra-violet spectrum of boron, their wave-lengths being:—

|         |          |
|---------|----------|
| 3451·4† | 2497·8†  |
| 3246·7  | 2496·88† |
| 2688·2  | 2267·03  |
| 2687·3  | 2266·47  |

In 1902 Exner and Haschek again took measurements of the lines in the ultra-violet spectrum of boron from a sample of boric acid obtained from Merck, and gave the wave-lengths of the three lines as 3451·49, 2497·79, and 2496·87.

In 1904 A. Hagenbach and H. Koenig (1905, Jena, G. Fischer; London, W. Wesley) published photographs of the boron spectrum in which the wave-lengths of the dominant lines are given as 3451, 2498, and 2497. The spark was taken between carbon poles with boric acid. Many other lines are shown, but the authors ascribe these to the electrodes.

In March, 1901, I was examining the silicon spectrum, using fused silicon electrodes, and a pair of lines were seen at about 2497 and 2498 which could not be found in any silicon spectrum photographed by other observers. I soon identified these strangers as lines given by a boron impurity in the fused silicon. A pure sample of fused silicon supplied by Johnson and Matthey did not show these lines.

## Properties of Boron.

Amorphous boron when pure is a fine dark brown powder. Its conductivity for electricity is very poor, and it is difficult to manipulate so as to get an induction spark through, as it is readily blown away. I could not fuse it in the arc.

Quite recently, Dr. Weintraub, of the West Lynn Research Laboratory, General Electric Co., U.S.A., has prepared boron in a solid state and chemically pure. Hitherto the physical properties of this element were unknown, notwithstanding the efforts of many chemists who had worked on the subject. Moissan, who came nearest to obtaining the pure element, only succeeded in getting it in the form of an amorphous powder. He said it was not possible to melt or volatilise boron in a carbon crucible or arc as it was changed into carbon boride, and concluded that boron passed from the solid to the gaseous state without becoming liquid.

Dr. Weintraub has not only obtained boron in a state of purity but has prepared it in a fused homogeneous form. His process consists in running one or more alternating current arcs, fed by a high potential transformer, between water-cooled or air-cooled copper electrodes, in a mixture of boron chloride with a large excess of hydrogen in a glass or copper vessel. The boron is thrown off in fine powder on to the walls of the vessel or agglomerates on the ends of the electrodes, where it grows in form of small rods. After a while the arc runs between two boron electrodes, and if the current is of proper value the rods melt down to boron beads which eventually fall off, whereupon the same process repeats itself.

The first specimens I received from Dr. Weintraub were deposited from a vaporous state from boron chloride and hydrogen in the manner already described. Subsequently I received some lumps of fused boron which had been prepared from magnesium boride obtained in the reaction between boric anhydride and excess of magnesium. The magnesium boride dissociates at a relatively low temperature (1200°), especially *in vacuo*, and with rapidity at 1500°. The fusion is effected between copper electrodes. Under the conditions of the experiment no disintegration takes place, and according to my informant, the affinity of copper for boron is so slight that it can be directly fused on to the electrode without being contaminated with copper. Another way of fusing boron is

\* A Paper read before the Royal Society, November 9, 1911.

† The lines so marked are the dominant lines.

in what Dr. Weintraub terms a mercury arc furnace, based on the fact that most refractory bodies, such as tungsten, tantalum, boron, &c., have no affinity whatever for mercury.

The fused lumps of boron obtained by the reaction between boron chloride and hydrogen were found by Dr. Weintraub to be quite pure, analysing from 99.8 to 100.2 per cent. The difference being due to errors of experiment, and perhaps to a trace of silica abraded from the agate mortar during pulverisation.

The boron prepared by fusing that obtained by the gas process is not quite so pure. The sample sent me contains about 97 per cent boron, the main impurities being nitrogen in the form of boron nitride, magnesium in the form of magnesium boride, a trace of iron, and a trace of carbon.

The most interesting property of solid boron is its extraordinary rise in electric conductivity with slight increase in temperature. A piece of fused boron measured by Dr. Weintraub, which at the room temperature (27° C.) had a resistance of 5,620,000 ohms, dropped to 5 ohms at a dull red heat.

Another noteworthy property of both the melted and agglomerated boron is extreme hardness. It comes next to the diamond in hardness, a splinter easily scratching corundum. Its fracture is conchoidal, and when melted no decided crystalline structure is seen. The agglomerated boron, deposited in the arc from boron chloride and hydrogen, is, on the contrary, highly crystalline. A rod of boron heated to whiteness before the blowpipe shows no sign of fusion, but the flame is coloured green, and when the cold rod is microscopically examined it is seen to be covered with minute globules of fused boric anhydride.

The first samples of boron under experiment were of the agglomerated variety, in the form of thin flakes deposited from the vaporous condition in the reaction already described. Several fragments were clamped together to form the electrodes.

It is not easy to get the spark to pass between cold boron poles owing to its high electrical resistance. When the two pole pieces are held in brass clips in front of the spectroscope the spark passes across from one clip to another; it is only when the boron poles get heated by the spark that they begin to conduct sufficiently to let the current pass. The light of the spark is somewhat feeble, and exposures from one to two hours are required to bring out with intensity the three dominant lines. Generally, when the boron electrodes are well heated the current assumes the form of a minute arc, starting from a luminous point at one edge of the pole, which soon becomes red-hot. Occasionally an intense yellow-green flame shoots from a corner which immediately fuses, but this only lasts a few seconds. After the current has passed for forty or fifty minutes an accumulation of boric anhydride causes a resistance to the current, and it then again begins to pass across between the brass clips.

The melted boron is easier to manipulate in the spectrograph. In the form of solid blocks, the electrodes do not get so hot, and very little oxidation takes place. The spark is of a faint apple-green colour, and when the poles have become sufficiently hot to carry the current it passes quietly for hours without change.

The spectrum of boron consists essentially of three lines, the wave-lengths of which, according to careful measurements made in the manner described in 1903, are 3451.50, 2497.83, and 2496.89 ("The Ultra-violet Spectrum of Radium," *Proc. Roy. Soc.*, 1903, vol. lxxii., p. 295) For easy comparison I give in a tabular form the wave-lengths of these lines measured by different observers:—

|                              |         |          |          |
|------------------------------|---------|----------|----------|
| Hartley (1883) . . . .       | 3450.3  | 2497     | 2496.2   |
| Rowland (1893) . . . .       | —       | 2497.821 | 2496.867 |
| Eder and Valenta (1893) . .  | 3451.3  | 2497.7   | 2496.8   |
| Exner and Haschek (1897) . . | 3451.4  | 2497.8   | 2496.88  |
| " " (1902) . .               | 3451.49 | 2497.79  | 2496.87  |
| Hagenbach and Korien (1908)  | 3451    | 2498     | 2497     |
| Crookes (1911) . . . .       | 3451.50 | 2497.83  | 2496.89  |

Besides these three lines two others of wave-lengths about 3274 and 3248 were seen on the photographs of each sample of boron, the agglomerated and the melted, the lines in the melted being the stronger. The fact that no other observer had noticed these lines, and their being of different intensities in the two samples, proved that they were due to some other element accidentally present. A run over my photographed spectra of the elements soon showed these lines to be the dominant copper lines, 3274.096 and 3247.688. A short time ago Sir Walter Noel Hartley (*Roy. Soc. Proc.*, vol. lxxxv., p. 271) traced the occurrence of these two copper lines in the spectrum from pure cadmium electrodes to the proximity of his laboratory to the overhead conductors of the Tram-lines. The condensation of the vapour of copper following the sparking at the rubbing contact yielded a dust of extreme tenuity, such as could not arise from mechanical abrasion of the solid metal. Sir Walter Noel Hartley found that the amount of copper passing between the sparking terminals sufficient to produce an impression of the copper lines on the photographic plate need not be more than from 0.001 to 0.0014 mgrm. This explanation could not apply to my own case, for no tram-lines are near the laboratory and nothing was going on that could give rise to a dust of copper. The atmosphere of my laboratory was perfectly free from any trace of copper, but the clips that hold the electrodes in front of the slit of the spectrograph were made of brass. When the spark first passes the boron is cold, and in that condition is a very bad conductor; consequently, some discharge may take place between the brass clips. After a little time, however, the boron gets hot enough to conduct the whole current.

To guard against such an accidental contamination, I made a pair of clips of pure gold for boron and other electrodes, and repeated the spectrographic tests with each sample of boron.

My reasons for selecting gold as the material for the clips were that it shows no lines near those in question of copper or aluminium; that it is a soft metal well adapted for clips holding hard bodies; that I had convenient blocks of it in a state of purity; and that all the lines of gold have been measured and mapped with accuracy.

The poles of agglomerated boron after sparking for two hours—using gold clips—gave a spectrum in which no trace of copper lines could be seen, whereas a similar experiment in which melted boron was used in the gold clips showed decided lines of copper and traces of magnesium.

Another pair of lines occurred in the neighbourhood of wave-lengths 3082 and 3093 in the spectrum given by the melted boron, but not in that of the agglomerated plates. This pointed to other impurities in the melted boron. On comparing these lines with spectra of other elements it was soon discovered that they were two of the dominant lines of aluminium, 3082.275 and 3092.818.

Experiments were now made to see if by greatly prolonged exposures in the spectrograph other boron lines could be brought out. Melted boron, sparked for seven hours in gold clips, gave a photograph showing many additional lines, which, however, were for the most part ill-defined air lines; four, however, occurring between wave-lengths 3930 and 3970, were definite and sharp although faint. These four lines might be due to boron, or to impurities, or they might be air lines. To ascertain if they were air lines a control experiment was tried by photographing the spectrum of pure tungsten sparked for seven hours. Tungsten was selected as the metal to put in comparison with boron because in its spectrum there is a blank space where the four lines brought out by long exposure of boron occurred. Had any of these four lines been brought out by long exposure in the tungsten spectrum it would show that they were common to both and not peculiar to boron. Close examination of the tungsten spectrum showed no trace of the four lines. The two photographs were enlarged, and most of the lines in common were found to be air lines.

It having been proved that the four lines in question were not air lines, the remaining alternatives were—



(a) they were boron lines, or (b) they were due to impurities in the boron.

To test the first hypothesis (a), that they were boron lines, several different specimens of boron, prepared by Dr. Weintraub and others, were examined in the spectrograph, and it was seen that the intensities of the lines varied considerably in comparison with known boron lines, being strong in some samples and almost absent in others. This pointed to hypothesis (b) as probably the true one, and a search was made for likely impurities having strong lines in the critical position.

Measurements were made of the four lines and their wave-lengths were calculated from those of adjacent iron lines, and the figures left no doubt that they were traces of the calcium lines 3933·825 and 3968·625 and the aluminium lines 3944·160 and 3961·674, Rowland's wave-lengths. This was confirmed by comparison with my photographed maps of the calcium and aluminium spectra.

The result of my work on boron is to show that its photographed spectrum consists of three lines; that the fourteen other lines given by J. M. Eder and E. Valenta, and the five other lines given by F. Exner and E. Haschek failed to record themselves on my photographs, notwithstanding the excessively long exposures I gave in the attempts to bring out additional boron lines.

#### A RE-DETERMINATION OF THE DENSITY AND COEFFICIENT OF LINEAR EXPANSION OF ALUMINIUM.\*

By F. J. BRISLEE, D.Sc., &c., Chief Chemist, British Insulated and Helsby Cables, Ltd.

THE increase in the use of aluminium for many technical purposes has rendered a re-determination of some of its physical constants necessary. The metal, as now placed upon the market, is in a high state of purity; but many of the earlier determinations of its physical constants were made upon specimens of aluminium of doubtful purity and unknown composition, which probably contained considerable quantities of iron, silicon, carbon, and oxide of aluminium, the oxide being mixed through the metal as an emulsion. Aluminium absorbs certain gases, when molten; hence the difficulty of obtaining sound castings; and blowholes would cause too low a value for the density to be obtained. The aluminium used in the determinations of the density and coefficient of linear expansion, described below, was obtained from (1) the Société Electrometallurgique Française, La Praz, Savoy, and (2) from the British Aluminium Company. A few specimens of re-melted scrap metal were used in one or two of the density determinations. All the metal used was carefully analysed, and the iron, silicon, the chief impurities present, were estimated. The iron was estimated by dissolving 10 grms. of the metal in caustic soda. The solution was allowed to stand, and the clear liquid syphoned off, water was then added, the precipitate again allowed to settle, and the clear solution removed by a syphon. The precipitate was then filtered off, thoroughly washed with water, dissolved in hydrochloric acid, precipitated with ammonium hydrate after oxidation, and weighed as oxide, or the hydrochloric acid solution was reduced and titrated with a N/10 solution of potassium dichromate. Repeated determinations, made upon the same sample, showed a good agreement between the two methods. The silicon was determined by the method of Otis-Handy. (Described in Lunge's "Chemisch-Technische Untersuchungsmethoden," ii., p. 789).

The analyses of the aluminium gave, as a mean of many determinations:—

|                 | S. E. M. F.<br>Per cent. | British Aluminium Co.<br>Per cent. |
|-----------------|--------------------------|------------------------------------|
| Silicon .. ..   | 0·26                     | 0·25                               |
| Iron .. ..      | 0·26                     | 0·23                               |
| Aluminium .. .. | 99·48                    | 99·52                              |
|                 | 100·00                   | 100·00                             |

#### The Density of Aluminium.

The specific gravity was determined upon the cast metal, as received, upon hard-drawn rod  $\frac{1}{8}$  in. diameter, and upon soft annealed rod  $\frac{1}{8}$  in. diameter. The determinations were made by both the ordinary method of weighing in air and water, and by employing the displacement method, using a 100 cc. flask, the latter method being employed for fine wire. The cast aluminium was cut into rectangular blocks, weighing from 20 to 30 grms. each; the round rod was cut into cylinders of about the same weight. The fine wire was cut into small pieces about an inch long; the weight used for a single determination was from 10 to 30 grms. The aluminium was carefully cleaned with petroleum ether, in order to remove grease, &c., which might have been taken up by the metal during working. The temperature of the water was taken at the time of weighing. The results obtained are given in Table I.

The density of re-melted aluminium is lower than the above, due probably to the fact that a certain proportion of iron and silicon are taken up during melting, and also to the fact that gases are absorbed while molten. The value found for the density of re-melted aluminium was  $16 \delta 16 = 2·687$ , or  $16 \delta 4 = 2·6821$ . The most probable value for the density of aluminium is  $2·708$  for cast metal, and metal upon which a large amount of work has not been done. The worked metal reaches  $2·72$ , in some of the above instances, but this value was obtained in only three determinations, and was not found for hard-drawn wire.

The above values differ from the values recorded in the literature, e.g., in Landolt and Börnstein ("Physikalisch-Chemische Tabellen"), and in a paper by Wilson (*Journ. Inst. Elect. Eng.*, 1901, xxxi., 332) in which a large amount of data are collected.

#### The Coefficient of Linear Expansion of Aluminium.

The coefficient of linear expansion was measured directly by determining the increase in length of a rod of the metal, about 1 metre long, when it was heated from 10° C. to 100° C. The apparatus is shown in the figure. It consists of a stout mild steel tube A, made of hydraulic tubing, which carries two heavy bronze clamps, B<sub>1</sub>, B<sub>2</sub>, which can be moved at will, and rigidly fixed in any position by means of clamping screws. B<sub>1</sub> carries a mild steel stop D, against which the end of the aluminium bar G rests when the determination is being made; the other (B<sub>2</sub>) carries a micrometer head C for measuring the change in length. The tube A is supported by the bronze supports M, N, which in turn were screwed on to the wooden blocks and base W<sub>1</sub>, W<sub>2</sub>, W<sub>3</sub>. A steady stream of water was kept flowing through A, the temperature of which was measured by the thermometer T<sub>4</sub>, placed in the glass vessel F. The temperature of the water did not vary more than 0·2° C. during the measurement, and the slight error caused thereby can be neglected. The aluminium bar was placed inside the water jacket K, and supported by a half tube, i.e., a brass tube cut out so as to form a shallow tray underneath the aluminium rod, the tube being complete only at the ends which carry the stop D and the stuffing-box H. The temperature of the bar was measured by the three thermometers T<sub>1</sub>, T<sub>2</sub>, T<sub>3</sub>. The change in length was measured by the micrometer C. Two micrometers were used, made by Messrs. Brown and Sharpe, and measured to 0·001 mm. and 0·0001 inch respectively. The increase in length of the bar G pushed the piston P through the stuffing-box H, and the change in length was then measured by the micrometer head C, the temperature remaining constant during

\* A Paper read before the Faraday Society, December 6, 1911.

TABLE I.

| Weight of aluminium.                                        | Weight of water displaced. | Source and condition of aluminium. | Temperature (°C.). | Specific gravity. |             |
|-------------------------------------------------------------|----------------------------|------------------------------------|--------------------|-------------------|-------------|
|                                                             |                            |                                    |                    | Uncorrected.      | Corrected.* |
| 31.3720                                                     | 11.5630                    | S.E.M.F. cast                      | 13                 | 2.7131            | 2.7094      |
| 29.8970                                                     | 11.0070                    | " "                                | 13                 | 2.7131            | 2.7094      |
| 29.8770                                                     | 11.0040                    | " "                                | 17                 | 2.7151            | 2.7098      |
| 31.3570                                                     | 11.5670                    | " "                                | 17                 | 2.7111            | 2.7057      |
| 15.3250                                                     | 5.6500                     | " "                                | 17                 | 2.7116            | 2.7051      |
| Mean specific gravity, $t \delta 4 = 2.7079$ , * corrected. |                            |                                    |                    |                   |             |
| 24.4570                                                     | 9.0130                     | B.A. $\frac{1}{8}$ rod, hard       | 22                 | 2.7137            | —           |
| 27.5290                                                     | 10.1440                    | " "                                | 22                 | 2.7135            | —           |
| 26.8310                                                     | 9.8850                     | " "                                | 22                 | 2.7143            | —           |
| 23.5180                                                     | 8.6660                     | " "                                | 22                 | 2.7137            | —           |
| 28.6890                                                     | 10.5700                    | " "                                | 22                 | 2.7143            | —           |
| 26.6040                                                     | 9.8020                     | " "                                | 22                 | 2.7141            | —           |

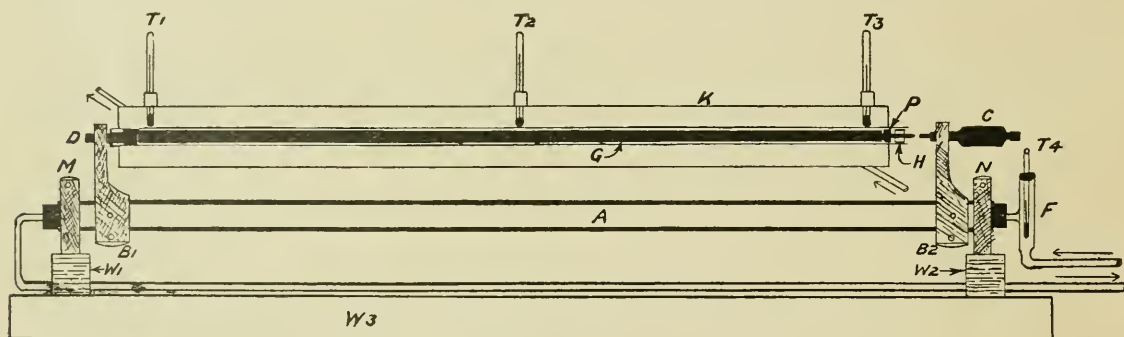
Mean specific gravity = 2.7139 uncorrected;  $t \delta 4 = 2.7052$  corrected.

|         |         |                            |    |        |        |
|---------|---------|----------------------------|----|--------|--------|
| 8.5220  | 3.1330  | S.E.M.F. $\frac{1}{8}$ rod | 17 | 2.7207 | 2.7153 |
| 7.5130  | 2.7610  | " "                        | 17 | 2.7211 | 2.7158 |
| 8.4930  | 3.1160  | " 0.08 wire                | 19 | 2.7256 | 2.7152 |
| 14.9350 | 5.5090  | " "                        | 16 | 2.7111 | 2.7060 |
| 28.3230 | 10.4656 | " "                        | 16 | 2.7063 | 2.7013 |
| 23.6630 | 8.7490  | " "                        | 16 | 2.7046 | 2.6996 |
| 20.4970 | 7.5570  | B.A. rod wire              | 14 | 2.7123 | 2.7084 |
| 24.4386 | 9.0320  | Wire                       | 14 | 2.7057 | 2.7018 |
| 25.3810 | 9.3560  | B.A. hard rod              | 19 | 2.7128 | 2.7064 |
| 25.3820 | 9.3610  | " "                        | 18 | 2.7115 | 2.7057 |
| 25.7370 | 9.4860  | Annealed rod               | 19 | 2.7131 | 2.7067 |
| 25.7374 | 9.4904  | " "                        | 18 | 2.7119 | 2.7061 |

Mean specific gravity,  $t \delta 4 = 2.7080$ † corrected.

\* Corrected for water at 4° C. and vacuum weighing,

†  $t \delta 4$  is the density at room temperature referred to water at 4° C.



the measurements. The determinations were made in the following way:—

The aluminium rods were cut so as to be approximately 1 metre in length. The ends were then turned up in a lathe, exactly at right angles to the long axis. The exact length was determined by comparison with a Whitworth standard steel bar 1 metre long, the difference being measured by a micrometer. The rod was then placed in position in the water-jacket K, which was well lagged with asbestos, the stop D, and the piston and the stuffing-box, P and H, fixed in position. Cold water was allowed to flow through the apparatus until the thermometers showed that the temperature was constant to within 0.1° C. The thermometers were calibrated from time to time so as to check the constancy of their indications. The thermometers showed that the temperature was practically constant during the actual determinations. The micrometer was then screwed down until the piston P pressed upon the end of the rod, and a reading of the position of the micrometer was then taken. A series of readings were taken of the thermometers and the micrometers, over a period of half-an-hour, so as to ensure that the temperature and

other conditions of the bar were constant. The cold water was then run out, and a steady current of steam was maintained, until the thermometers showed that a constant temperature was reached. The micrometer C was again screwed down on to P, and the reading taken. A series of readings were taken of both micrometer and thermometers. The bar was kept at the temperature of the steam for half-an-hour, and comparative tests showed that temperature equilibrium between the steam and metal was established in ten to fifteen minutes. At the completion of the measurement the steam was shut off, and cold water circulated through the apparatus. When the initial temperature was reached, the first readings of the micrometer were checked. The readings at the higher temperature were repeated by again heating to the temperature of steam. It was found that successive determinations made with the same bar agreed to within 0.2 to 0.3 per cent. During the whole of the measurements the temperature of the tube A was kept constant by a steady current of water, and the bronze clamps B<sub>1</sub> and B<sub>2</sub> were shielded from radiant heat by thick asbestos screens. The temperature of the bar, as indicated by the thermometers T<sub>1</sub>, T<sub>2</sub>, T<sub>3</sub>,



showed that a constant temperature was maintained in the jacket to within  $0.1^{\circ}\text{C}$ .

The results give—

$$\beta = 2.432 \times 10^{-5} \pm 0.0036 \times 10^{-5}$$

as a mean of the seventeen determinations given in Table II. The mean probable error was calculated from the formula—

$$\frac{\Sigma d^2}{N(N-1)},$$

where  $\Sigma d^2$  is the sum of the squares of the differences between the mean and each determined value of  $\beta$ , and  $N$  is the number of determinations.

TABLE II. — *Hard-drawn Aluminium.*

| Length of bar<br>in cm. = $l$ . | Temperature rise,<br>$^{\circ}\text{C.} = (t_2 - t_1)$ . | Increase in length<br>in mm. = $\Delta l$ . | $\beta = \frac{\Delta l}{l(t_2 - t_1)}$ . |
|---------------------------------|----------------------------------------------------------|---------------------------------------------|-------------------------------------------|
| 100.2664                        | 87.5                                                     | 2.117                                       | $2.413 \times 10^{-5}$                    |
| 100.1700                        | 88.1                                                     | 2.119                                       | 2.406 "                                   |
| 100.2664                        | 88.3                                                     | 2.130                                       | 2.406 "                                   |
| 100.2664                        | 88.0                                                     | 2.167                                       | 2.456 "                                   |
| 100.1920                        | 89.4                                                     | 2.175                                       | 2.428 "                                   |
| 100.1920                        | 89.9                                                     | 2.210                                       | 2.454 "                                   |
| 100.1692                        | 98.02                                                    | 2.225                                       | 2.441 "                                   |
| 100.1692                        | 91.0                                                     | 2.220                                       | 2.436 "                                   |
| 100.1900                        | 89.3                                                     | 2.175                                       | 2.431 "                                   |
| 100.1900                        | 88.7                                                     | 2.167                                       | 2.438 "                                   |
| 100.2560                        | 87.8                                                     | 2.162                                       | 2.455 "                                   |
| 100.2560                        | 90.6                                                     | 2.207                                       | 2.430 "                                   |
| 100.2560                        | 90.5                                                     | 2.197                                       | 2.430 "                                   |
| 100.0560                        | 89.3                                                     | 2.173                                       | 2.430 "                                   |
| 100.0560                        | 90.1                                                     | 2.180                                       | 2.420 "                                   |
| 100.2498                        | 89.5                                                     | 2.185                                       | 2.436 "                                   |
| 100.2498                        | 91.4                                                     | 2.225                                       | 2.430 "                                   |

TABLE III. — *Annealed Aluminium.*

|          |      |       |                        |
|----------|------|-------|------------------------|
| 100.1055 | 88.6 | 2.190 | $2.469 \times 10^{-5}$ |
| 100.2543 | 88.7 | 2.187 | 2.459 "                |
| 100.2543 | 88.5 | 2.187 | 2.465 "                |
| 100.2591 | 89.7 | 2.217 | 2.465 "                |
| 110.2405 | 89.8 | 2.216 | 2.461 "                |
| 100.2405 | 90.4 | 2.225 | 2.453 "                |
| 100.2405 | 89.2 | 2.193 | 2.453 "                |
| 100.1075 | 88.5 | 2.170 | 2.450 "                |
| 100.1075 | 88.7 | 2.185 | 2.461 "                |
| 100.1075 | 88.7 | 2.190 | 2.466 "                |
| 100.1075 | 89.2 | 2.200 | 2.464 "                |
| 100.2403 | 89.6 | 2.202 | 2.452 "                |
| 100.0810 | 89.0 | 2.180 | 2.447 "                |
| 100.0810 | 90.0 | 2.205 | 2.433 "                |
| 100.2498 | 89.5 | 2.197 | 2.438 "                |
| 100.2498 | 90.5 | 2.210 | 2.436 "                |

The general mean of the determinations given in Table III., sixteen in number, is—

$$\beta = 2.454 \times 10^{-5} \pm 0.0028 \times 10^{-5}.$$

From the two series of measurements (Tables II. and III.) the variation in length of an aluminium rod can be calculated from the formulæ—

$$\text{Hard-drawn aluminium} \dots L_t - L_{t_1} (0.00002432 t)$$

$$\text{Annealed aluminium} \dots L_t - L_{t_1} (0.00002454 t)$$

between the limits of temperature  $0^{\circ}$  to  $100^{\circ}\text{C}$ .

#### Sources of Error in the Determinations.

The measurements above recorded could all be reproduced by repetition of the heating and cooling to within  $0.2$  to  $0.3$  per cent. Since the micrometers were capable of being read to  $0.0025$  mm., and since the total expansion measured was about  $2.2$  mm., the maximum error of measurement was  $0.13$  per cent.

The error in the temperature readings was not greater than  $0.1^{\circ}\text{C}$ . The correction of the thermometers was effected by checking their indications by substances of

known melting- and boiling-points. The corrected temperature differences were used in calculating  $\beta$ .

The errors due to the slight expansion of the stop D and the piston P were found to be negligible by varying the length of these two parts. The length of D and P together was 3 cm. in one series of measurements, and 15 cm. in another series. The results were practically identical, as will be seen from the following figures:—

|                               | Shorter ends.            | Longer ends.             |
|-------------------------------|--------------------------|--------------------------|
| Length of bar in cm. . . .    | 100.2403                 | 100.1075                 |
| Temperature rise . . . .      | $89.6^{\circ}\text{C}$ . | $88.5^{\circ}\text{C}$ . |
| Increase in length in mm. . . | $2.202$                  | $2.170$                  |
|                               | $2.452 \times 10^{-5}$   | $2.450 \times 10^{-5}$   |

The temperature rise of these parts was only small, and, owing to the shortness of the ends, the error caused was not greater than  $0.003$  mm. The results obtained are somewhat higher than the recorded values of  $\beta$ . Fizeau (*Comptes Rendus*, 1869, lxxviii., 1125; *Pogg. Ann.*, 1869, cxxxviii., 28) found  $2.313 \times 10^{-5}$  up to  $40^{\circ}\text{C}$ . and  $2.336 \times 10^{-5}$  up to  $50^{\circ}\text{C}$ ., while Le Chatelier (*Comptes Rendus*, 1889, cviii., 1096), working with much purer aluminium, found  $2.46 \times 10^{-5}$  up to  $63^{\circ}\text{C}$ .

The coefficient of linear expansion was invariably found to be slightly higher for annealed aluminium than for hard-drawn aluminium, but the third significant figure is somewhat uncertain, owing to the errors of the determination. The mean value for  $\beta$ , calculated from forty-eight determinations made upon hard and annealed aluminium, was—

$$\beta = 2.450 \times 10^{-5} \text{ per degree centigrade,}$$

or  $1.361 \times 10^{-5}$  per degree Fahrenheit.

The above measurements were made upon twelve different rods, and the results were reproduced several times before they were considered reliable.

The accuracy of the expansion apparatus was tested by measuring the expansion of a bar of pure high-conductivity copper. The value obtained was  $1.758 \times 10^{-5}$ , a value which is practically identical with that given by Zakrzewski (*Krak. Anz.*, 1889, No. 19), who found  $1.753 \times 10^{-5}$ .

## CHEMICAL NATURE OF SOIL ORGANIC MATTER.\*

By OSWALD SCHREINER and EDMUND C. SHOREY.

### Introduction.

EVERY soil investigator, whether it be the chemist, bacteriologist, or physicist studying some special problem, or the agronomist dealing with the general relation of soils to crops, sooner or later encounters difficulties that have their origin in the lack of knowledge of the chemical composition of the organic matter of the soil.

Some organic matter is essential to make a soil of what would otherwise be pulverised and more or less hydrolysed rock, and while there are some soils capable of growing crops that contain very small quantities of organic matter, on the whole the quantity of this material in average soils is considerable. Analyses have shown that the average organic content of the soils of the United States is  $2.06$  per cent and of subsoils  $0.83$  per cent (Cameron, *Journ. Am. Chem. Soc.*, 1905, xxvii., 256).

This means 28 tons of organic matter per acre in the first 8 inches of soil and 50 tons in the soil and subsoil together to the depth of 2 feet.

The varied sources of this organic matter and the different classes of compounds that are known to result from the decomposition of this material have been fully discussed in a previous publication (*Bull.* 53, Bureau of Soils, U.S. Dept. Agr., 1909, p. 9), and it is necessary to state here simply the fact that this organic matter may have its

\* Bulletin No. 74, U.S. Department of Agriculture, Bureau of Soils.

source in the remains of any plant or animal, and the resulting compounds may be those that were in the living tissues and have resisted decay, those that result from a splitting or degradation of complex bodies present in the living plant or animal, or compounds arising through changes brought about by micro-organisms, and that nearly all classes of organic chemical compounds known may be represented.

Two views regarding the soil organic matter are at present current in agricultural literature. The first is some modification of the view of Mulder (1849) ("The Chemistry of Vegetable and Animal Physiology," trans. by Fromberg, 1849, p. 146), "that at present seven different organic substances are known to exist in the soil. They are crenic acid, apocrenic acid, geic acid, humic acid and humin, ulmic acid and ulmin."

This view, modified to the extent that some such body as humic acid, differing perhaps in different soils, but having the same general properties, makes up the humus and the greater portion of the organic matter of all soils is accepted by many agronomists and chemists. The acceptance of this view, which originated in the days when there was no organic chemistry in the present meaning of the term, can be attributed to two factors which have tended to retard the progress not only of agricultural chemistry but of other branches of science as well. These are the tendency to simplify or unify what proper thought would show to be complex; and second, the too prevalent habit of some investigators and most compilers of repeating or quoting scientific statements or deductions which have been made in the first place on wholly insufficient grounds. This view of soil organic matter has been fully discussed in a previous bulletin (*Bull.* 53, Bureau of Soils, U.S. Dept. Agr., 1909, p. 21), and it is not necessary to repeat that discussion here, for one of the results of the present paper is to show that the bodies that Mulder regarded as simple compounds related to each other are really made up of a large number of chemical compounds not necessarily related.

In strong contrast to this view of the simple composition of the soil organic matter is the second view current in agricultural literature, that the material is of a very complex nature, regarding which very little is known. Little fault can be found with this statement in itself, but it is often made in such a way as to convey the impression that not only do we know little regarding its complexity, but that it is almost hopeless to attempt any investigation of it. There is, moreover, seldom coupled with this confession of ignorance any appreciation of the importance of a thorough knowledge of the chemical composition of this important soil constituent.

In considering the importance of the organic matter of the soil it should be borne in mind that it is material that is the result of change, and that much, perhaps all of it, is susceptible of still further change; that is, it is in a transition stage. The changes which it has undergone and the changes which it may still undergo are determined by a number of factors, chief of which are moisture, aeration, character of micro-organisms, and mutual relation of the organic compounds and the mineral constituents. These factors are many of them influenced or controlled by the cultural methods, including fertilising, drainage, irrigation, inoculation, &c., used in practical agriculture. While it is true that the soil, viewed from whatever point, presents dynamic problems, the study of the organic matter without doubt presents such problems in greatest complexity, but at the same time problems most susceptible of solution, once the character of the material is known.

This view of the importance of soil organic matter concerns the agronomist and the farmer, but when the work of the special investigator is considered the need of definite knowledge is even more strongly emphasised. It is not necessary that the practical agriculturalist should know the chemical names or formulæ of the organic compounds in the soil, but to the scientific investigator, to whom the farmer looks for the "why" of agricultural operations,

such knowledge is necessary because it carries with it a knowledge of their properties. There can be intelligent chemical treatment of any material only when the chemical nature of the material treated is known. The treatment to which soil organic matter is subjected under cultural methods is in part at least chemical treatment in that such methods induce chemical changes. The operations of irrigation, conserving of moisture by mulches, aeration by cultivation, inoculation with cultures of bacteria, addition of organic and green manures, are all common agricultural methods used by farmers, and they are also operations that influence the chemical changes which soil organic matter undergoes.

The influence of the organic matter of the soil may be considered under four heads: Its effect on the crop, its effect on the bacteria and fungi of the soil, its influence on the physical properties of the soil, and its relation chemically to the mineral ingredients of the soil.

It is a well-established fact that some chemical compounds which occur in plants and may get into the soil are harmful to growing plants when presented in water solution to the roots (*Bull.* 47, Bureau of Soils, U.S. Dept. Agr., 1907). It has also been shown that some organic compounds that occur in soils and have been isolated from them are also harmful to growing plants under these conditions (*Bull.* 53, Bureau of Soils, U.S. Dept. Agr., 1909). On the other hand, plants may take up other organic compounds when presented to their roots in water solution without injury to the plant, or in the case of some nitrogenous bodies, with benefit. Now, while the organic matter of soils is for the most part little soluble in water, a water extract of soils always contains some organic matter. In consequence organic compounds have always to be considered as a portion of the material in the nutrient solution supplied to crops growing in the soil.

The chief function of bacteria and fungi is to act on the higher organic compounds which make up living organisms and convert them into simpler compounds. In other words, these higher compounds are the food of the micro-organisms. The simpler compounds resulting from the activity of the fungi and bacteria commonly spoken of as the products of decay or fermentation, are, in part at least, still organic substances and help to make up this portion of the soil. No fact regarding bacteria is better established than that they are influenced not only in habit of growth but also in the character of the compounds produced, by the chemical composition of the medium in which they are grown and are generally intolerant of the presence of an excess of their own by-products. The soil organic matter impregnated with the soil solution is then the culture medium in which soil micro-organisms have to grow and contains also the products of their growth. Bacteria, the activity of which is beneficial to crops, may fail to flourish because the food supplied them is not suitable or because their own products or the products of other forms hinder their growth. On the other hand, the activity of harmful bacteria, fungi, or protozoa may be stimulated by an abundant supply of suitable food. The necessity, then, of some chemical knowledge of this culture medium and by-products in any study of the mutual relation of soil micro-organisms to each other or to crops is apparent.

The properties of soils generally included under the term "physical," such as water-holding power, heat conductivity, absorption, and granulation, are universally recognised as potent factors in determining the character of a soil and its adaptability to the growing of crops. In considering these factors the tendency has been to consider the soil simply as an aggregate of mineral particles of different sizes, and consequently of different surface area, and to correlate the varying physical properties with this variation. That this view is wholly inadequate is evident, for solid organic matter may also be present in particles of different sizes, and these may have different physical properties due not only to variation in size, but probably in even greater degree to differences in chemical composition and structure. Furthermore, the organic



matter may, and in fact generally does, play an intimate part in the behaviour of the mineral particles, entering into chemical combination, coating them or cementing them together. The organic matter becomes, therefore, of the greatest importance in its influence on the great controlling factors in crop production, such as the solubility of the soil minerals, the physical structure of the soil granules, and the water-holding power of soils. To illustrate this, there was found in California a soil which could not be properly wetted, either by rain, irrigation, or movement of water from the subsoil, with the result that the land could not be used profitably for agriculture. On investigation it was found that this peculiarity of the soil was due to the organic matter, which when extracted had the properties of a varnish, repelling water to an extreme degree. The soil, once freed of this ingredient, had a high water-holding power. From other soils bodies of a waxy nature have been isolated, and it can thus be seen that certain kinds of organic matter are important as the cause of the low water-holding power of some soils, although in general the presence of the organic remains of plants increases the power of soils to hold moisture—an important factor in crop production. It is evident, then, that there can be intelligent study of the influence that the organic matter of the soil has on its physical properties only when the chemical identity of its several components is known.

The great majority of organic chemical compounds are reactive towards inorganic compounds, acids, bases, and salts. Organic acids can form salts with mineral bases or double salts with mineral salts. Organic bases form salts with mineral acids, and quite a number of organic compounds combine both acid and basic properties and form organic compounds with both mineral acids and bases. Such being the case, there necessarily exists a mutual relation between the organic compounds in the soil and the mineral particles which form its foundation. Some of the acids isolated from the soils could not exist free for any time in a soil containing free bases or salts of weak acids, such as carbonic acid, and there is abundant evidence that many of the organic compounds exist in the soil in mineral combination. In fact, the relation between the organic and mineral particles of the soil is so intimate that any differentiation of soil chemistry into organic and inorganic should not be used as the basis of any theory or line of argument regarding soil phenomena or soil treatment.

In *Bulletin* 53 of this bureau the methods of isolating four organic compounds from soils was described and their properties given. The isolated compounds were:—Dihydroxystearic acid,  $C_{18}H_{36}O_4$ ; picoline carboxylic acid,  $C_7H_7O_2N$ ; agroceric acid,  $C_{21}H_{42}O_3$ ; and agosterol,  $C_{26}H_{44}O.H_2O$ .

Since the publication in this *Bulletin* of a review of the literature bearing on the nature of the organic matter of the soils, there have appeared several papers on the methods of humus determination and on the nature of the nitrogenous compounds resulting from the decomposition of the humus material with acids. None, however, have added any definite information regarding the identity of any compounds in the organic portion of the soil. A paper by Miklauz is a valuable contribution to our knowledge of the variable character of humus material ("Beiträge zur Kenntniss der Humussubstanzen," *Zeit. f. Moorkultur und Torfverwertung*, 1908, 285). This paper deals for the most part with the solubility of humus bodies in different solvents and the differences in the elementary composition of the separate fractions obtained by this means.

With the idea of the general importance of a greater knowledge of the chemistry of the soil organic matter in mind, and with the view of furnishing more specific information of value in attempting to solve some of the problems presented by differences in or lack of fertility of soils, the work of which the present paper is a report was undertaken.

The work deals with a number of soils selected because of some problem presented by field observation, although these problems are not dealt with here. No one soil has been studied exhaustively, nor has there been any attempt to account for all of the organic matter in the soil in identified compounds. In some cases, however, this is approached by the sum of the identified compounds and separated fractions, the composition and properties of which are known but the identity of which has not as yet been established.

Two general methods have been used in the preliminary treatment of soils to obtain a solution from which to isolate organic compounds. These were the treatment with dilute alkali as in previous work and treatment with boiling 95 per cent alcohol. In several cases the same compounds were obtained by both methods.

It is quite evident that the compounds isolated from soils and described in this *Bulletin* could not have been formed by any deep-seated change effected by the alkali or alcohol in the method of extraction. The alkali used was dilute, 2 per cent, the treatment was at room temperature and for a short time only, and the compounds isolated are not known to be formed by decomposition of more complex organic material by any such treatment. This treatment does effect changes in some of the organic matter of soils, but the material changed and the resulting compounds are not dealt with in this publication.

The after treatment of these solutions was also along two general lines. First, general treatments used in the separation or isolation of organic compounds, for the most part shaking out with immiscible solvents and precipitating with metallic salts, and, second, the direct search for certain compounds by methods already used for the isolation of such bodies in biochemical work.

When definite compounds were obtained by the general search, where the method used gave little or no clue to the identity of the compound obtained, it was necessary to obtain sufficient of the body to determine its elementary composition and its general properties in order to establish its identity. When, however, a compound was obtained as the result of a direct search by an approved method, the correspondence of the properties, such as melting-point, crystalline appearance, solubility, &c., of the compound obtained and the compound sought has been deemed sufficient to establish its identity.

The compounds obtained have been classified and described according to the group of chemical compounds to which they belong. In some cases compounds belonging to two or more groups have been obtained as steps in one method, and if treated wholly from the point of view of method these would be described together. Since, however, the number of bodies isolated is constantly increasing, the classification according to method would soon result in confusion, and the chemical classification has been adhered to even when there was but one representative of a group. When compounds isolated have been obtained at different stages in the same method of treatment the fact is made clear in the text.

(To be continued)

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Behaviour of Metallic Hydrates towards Alkylene-diamine Solutions.—Wilhelm Traube.—Copper hydroxide is less soluble in aqueous solutions of primary aliphatic amines than in ammonia, but 1,2-diamines containing two primary amino-groups are excellent solvents for it. One molecular weight of copper is always dissolved for every two molecular weights of diamine in the solution. Probably a cupric-ethylene-diamine hydroxide of formula  $[Cu(C_2H_5N_2)_2](OH)_2$  is present in the solution, but the author has not succeeded in isolating it. The hydrates of nickel, cobalt, zinc, and cadmium, and the oxides of silver and mercury are also taken up by alkylene diamines in definite molecular proportions.—*Berichte*, xlv., No. 16.

## PROCEEDINGS OF SOCIETIES.

## CHEMICAL SOCIETY.

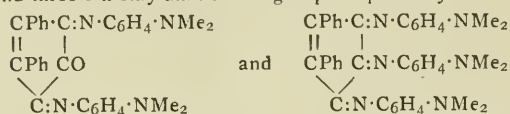
Ordinary Meeting, December 7th, 1911.

Dr. M. ONSLOW FORSTER, D.Sc., Ph.D., F.R.S.,  
Vice-President, in the Chair.

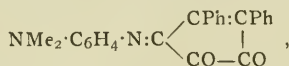
(Concluded from vol. civ., p. 316).

316. "*Diphenylcyclopentenone*." By SIEGFRIED RUHE-MANN and WILLIAM JOHNSON S. NAUNTON.

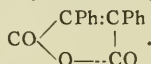
With the view of preparing cyclic triketones with three adjacent ketonic groups similar to triketohydrindene, 3 : 4-diphenylcyclopentenone (Japp and Lander, *Trans.*, 1897, lxxi., 131) was treated with *p*-nitrosodimethylaniline. This reaction yields two condensation products with two and three dimethylaminoanilo-groups respectively:—



Both compounds on hydrolysis with mineral acids yield 5-dimethylaminoanilo-3 : 4-diphenylcyclopentene-1 : 2-dione:—



which on heating with concentrated hydrochloric acid at 130–140° forms diphenylmaleic anhydride:—



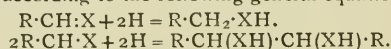
5-Dimethylaminoanilo-3 : 4-diphenylcyclopentene-1 : 2-dione when treated with bromine gives a yellow bromo-derivative,  $\text{C}_{25}\text{H}_{19}\text{O}_2\text{N}_2\text{Br}$ , but with an excess of the halogen an unstable *perbromide* is produced, which on boiling with alcohol decomposes to yield the same yellow monobromo-derivative along with a scarlet dibromo-compound,  $\text{C}_{25}\text{H}_{18}\text{O}_2\text{N}_2\text{Br}_2$ .

With fuming nitric acid the substance forms a scarlet dinitro-derivative,  $\text{C}_{25}\text{H}_{18}\text{O}_2\text{N}_2(\text{NO}_2)_2$ ; on reduction with zinc dust and acetic acid it furnishes a colourless compound,  $\text{C}_{25}\text{H}_{22}\text{O}_2\text{N}_2$ .

5-Dimethylaminoanilo-3 : 4-diphenylcyclopentene-1 : 2-dione is deep red or orange, according to whether it separates from concentrated or dilute alcoholic solutions. It forms salts, which, however, readily dissociate with water. It, further, has the remarkable property of being transformed into a colloid on the addition of water to its solutions in absolute alcohol or acetone. This spontaneously liquefies, with separation of crystals in the course of two or three days. Neither the bromo- nor the nitro-derivatives show this phenomenon.

317. "*Electrolytic Reduction*. Part V. *Benzylidene Bases*." By HERBERT DRAKE LAW.

A series of compounds were reduced by the electrolytic method in continuation of similar experiments with the aromatic aldehydes. The results agreed closely with those previously obtained. Two classes of compounds were formed, according to the following general equations:—



Thus benzylidene-*p*-toluidine yielded benzyl-*p*-toluidine, di-*p*-toluidinodibenzyl, and a green resin. The relative quantity of each constituent varied with the conditions of the experiment, but followed the same rules as those previously given in the case of benzaldehyde. The quantities of each substance formed varied very considerably with a change in constitution. The resin formed diminished as the formula of the reduced substance approached the most symmetrical arrangement of the substituted groups.

318. "*The Porosity of Iron and its Relation to Passivity and Corrosion*." By JOHN ALBERT NEWTON FRIEND.

The author showed that:—(1) The surface of iron is slightly porous, so that when the metal is immersed in certain solutions the latter are absorbed to a minute extent. (2) The passivity induced by immersion of iron in alkaline solutions, such as those of sodium and potassium hydroxides, is due to absorption of small quantities of these alkalis within the pores of the metal. (3) There are thus more kinds of passivity than one.

319. "*Molecular Rotatory Power in Normal Homologous Series*. Part I. *Optically Active Derivatives of the Higher Aliphatic Alcohols and Acids*." By THOMAS PERCY HILDITCH.

The variation of different types of physical properties in consecutive members of an homologous series was discussed, and it was pointed out that, whilst the more additive properties increase in arithmetical progression on ascending such a series, certain essentially constitutive properties tend in these circumstances to arrive at a constant value.

A survey of the existing data on the molecular rotatory powers of optically active homologues shows that here also, although hitherto only the first few members of series of this type have been available, this function nevertheless reaches in many cases an approximately constant figure, characteristic of the optically active series concerned; moreover, those series which do not yield constant values for  $[\text{M}]_D$  almost invariably contain strongly unsaturated groups.

The author therefore proposes to investigate the homologues of higher molecular weight of some apparently irregular series in order to determine whether the presence of unsaturation is here a disturbing factor in the lower members. To this end it was necessary in the first place to ensure that, in series the lower members of which rapidly attained constancy of molecular rotatory power, the homologues of high molecular weight should maintain their "series constant" of molecular rotation.

Investigation of the *l* menthyl esters, and brucine and cinchonine salts of myristic, palmitic, and stearic acids, and of the hydrogen camphorates and camphor-*B*-sulphonates of cetyl and myricyl alcohols, showed that, within narrow limits, the molecular rotatory powers of the normal aliphatic esters of *l*-menthol, *d*-camphoric acid, and *d*-camphor-*B*-sulphonic acid, and of the normal aliphatic salts of brucine and cinchonine, become numerically constant in each series after the first few members are passed.

320. "*Molecular Rotatory Power in Normal Homologous Series*. Part II. *The Menthyl Esters of the  $\alpha$ -Bromoaliphatic Acids*." By HAROLD CHRISTOPHER and THOMAS PERCY HILDITCH.

The effect of introducing an unsaturated group in close proximity to the carboxyl residue of a series of optically active normal aliphatic esters has been studied by the authors in connection with the problem of the disturbing effect of unsaturation referred to in the preceding paper.

The  $\alpha$ -bromo-derivatives of the aliphatic esters of *l*-menthol were employed in the present investigation on account of the ease with which these compounds may be obtained in the pure condition.

It was found that whilst the first two members of the series (menthyl bromoacetate and  $\alpha$ -bromopropionate) possessed molecular rotatory powers markedly above the normal, the anomaly rapidly declined to a minimum, slightly sub-normal value, thereafter rising very much more gradually to an approximately constant value (in the case of menthyl  $\alpha$ -bromomyristate and  $\alpha$ -bromopalmitate). The final constant molecular rotations appeared to be a very few degrees in excess of those of the corresponding members of the saturated non-substituted aliphatic menthyl esters.



321. "Note on Methyl-*n*-tridecyl- and Methyl-*n*-pentadecyl-carbinols and the corresponding Ketones." By ROBERT HOWSON PICKARD and JOSEPH KENYON.

In a recent communication (*Trans.*, 1911, xcix., 45) the authors have described the resolution into their optically active components of the members of the series of carbinols from methylethylcarbinol to methyl-*n*-undecylcarbinol. It was intended to continue the series so as to include methyl-*n*-tridecyl- and methyl-*n*-pentadecylcarbinols, but it has been found that the method of bringing about the resolution of the various members of the series fails in the case of these carbinols, containing fifteen and seventeen carbon atoms respectively. This note contains a short description of the compounds isolated during the course of the experiments, and also shows that the catalytic method with thorium oxide (Senderens, *Comptes Rendus*, 1909, cxlv., 995) can be used for the formation of ketones, even when they contain many carbon atoms.

Methyl-*n*-tridecyl Ketone,  $\text{CH}_3 \cdot \text{CO} \cdot \text{C}_{13}\text{H}_{27}$ .—Myristic acid (300 grms.) dissolved in glacial acetic acid (2400 grms.) was passed at an hourly rate of 50 cc. through a Jena-glass tube containing thorium oxide, and heated to 400°. The products of the reaction were condensed, dissolved in ether, and washed with a solution of sodium hydroxide until free from acid. Myristic acid (125 grms.) was recovered from the washings, mixed afresh with glacial acetic acid, and again treated. When the products from the two operations were fractionally distilled, 200 grms. of methyl-*n*-tridecyl ketone were obtained. The residue in the flask when re-crystallised from ethyl alcohol yielded 30 grms. of myristone, which melted at 75–76°.

Methyl-*n*-tridecyl ketone boils at 184°/20 mm., and on cooling sets to a soft mass of crystals, which melt at 37°. It readily forms the semicarbazone, which crystallises from ethyl alcohol in needles melting at 126.5°. (Found,  $N = 15.0$ . Calc.,  $N = 14.8$  per cent).

Methyl-*n*-tridecylcarbinol,  $\text{CH}_3 \cdot \text{CH}(\text{OH}) \cdot \text{C}_{13}\text{H}_{27}$ , is readily obtained when the corresponding ketone is reduced by sodium in 96 per cent alcoholic solution, little, if any, pinacone being formed. It boils at 181–183°/19 mm., and on cooling sets to a crystalline mass, which melts at 38–39°.

The hydrogen phthalate crystallises from light petroleum in pearly leaflets, and melts at 61–62°. (The purity of each of the acid esters described in this note was ascertained by titration of their alcoholic solutions with a standard solution of sodium hydroxide). The brucine salt crystallises from acetone in needles, which, when dried in the air, melt at 80–85°, but after desiccation in a vacuum or after heating at 105° for a few minutes they melt at 172–175°. After two re-crystallisations, on polarimetric examination:—

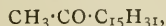
1.0136, made up to 20 cc., with ethyl alcohol, gave  $a - 6.25^\circ$ , whence  $[\alpha] - 61.66^\circ$ .

The strychnine salt crystallises from chloroform and acetone in hair-like needles, melts about 130°, and has  $[\alpha]_D - 52.6^\circ$  when dissolved in chloroform. The hydrogen phthalate obtained from the purest specimen of these salts was in each case found to be quite inactive when examined in the polarimeter.

The hydrogen succinate crystallises from light petroleum in nacreous leaflets, which melt at 60–61°. The brucine salt is a wax, and unsuitable for fractional crystallisation.

The corresponding derivatives of heptadecane were obtained by similar methods.

Seventy-nine grms. of methyl-*n*-pentadecyl ketone,



were obtained from 112 grms. of palmitic acid. It boils at 197°/12 mm., crystallises from ethyl alcohol in pearly leaflets melting at 48°, and can be regenerated unchanged from the semicarbazone, which crystallises from dilute ethyl alcohol in very small needles melting at 125.5°.

Methyl-*n*-pentadecylcarbinol boils at 230°/16 mm., forms indefinitely shaped crystals, and melts at 46°. The

hydrogen phthalate separates from light petroleum as a mass of needles, which melt at 50–51°. The hydrogen succinate separates from light petroleum in a micro-crystalline condition, and melts at 64–65°. The brucine salts of each of the esters were prepared and re-crystallised several times, but no ester could be obtained which exhibited any trace of optical activity.

322. "An Experimental Investigation of the Bleaching Process." By SYDNEY HERBERT HIGGINS.

Solutions of the hypochlorites of lithium, sodium, and potassium prepared from bleaching powder solution by precipitation with solutions of the alkali sulphates or carbonates have identical bleaching properties; the bleaching efficiencies of these solutions are almost equal to that of the original bleaching powder solution. Curves showing (1) the evolution of oxygen from hypochlorite solutions and from solutions of sodium peroxide in contact with copper oxide; (2) the rate of bleaching of solutions of hypochlorites and of sodium peroxide; (3) the rate of oxidation of oxalic acid by potassium permanganate and the rate of liberation of iodine from potassium iodide by acidified sodium peroxide solution (Harcourt and Esson, *Phil. Trans.*, 1866, clvi., 193), point to the conclusion that the actions in all these cases are similar, that is, unimolecular. Hypochlorites therefore bleach because of their readiness directly to produce nascent oxygen. Those substances which accelerate the evolution of oxygen from solutions of hypochlorites or of peroxides also assist the evolution of that gas when they are heated along with potassium chlorate; hence it is taken that the main action in the latter case is a unimolecular one. Chlorine water is a much weaker bleaching agent than solutions of hypochlorites; therefore the bleaching action of the latter cannot be due to the generation of free chlorine as stated by Taylor (*Trans.*, 1910, xcvi., 2541). Chlorine water probably owes its bleaching properties to the presence of hypochlorous acid in solution. The proof that the production of chlorine from bleaching powder solution and the stimulation of the bleaching action of that solution have no connection with one another has led the author to consider the two questions separately. In pursuit of this line of argument he gave further experiments supporting previous conclusions (compare Taylor, *Proc. Chem. Soc.*, xxvii., 243).

323. "The Direct Esterification of Saturated and Unsaturated Acids." By EBENEZER REES THOMAS and JOHN JOSEPH SUBBOROUGH.

The esterification of a number of saturated and unsaturated organic acids has been studied by heating the acid with a large excess of pure ethyl alcohol at 100° in sealed tubes for given periods, and titrating the amount of free acid left.

The results show that an  $\alpha\beta$ -olefine linking has a retarding effect, except when the unsaturated acid is a very much stronger acid than its saturated analogue, for example, methyl hydrogen maleate, which is some two hundred times as strong an acid as methyl hydrogen succinate. In such a case the olefinic acid is esterified more rapidly than the corresponding saturated acid.

A  $\beta\gamma$ -unsaturated acid is usually esterified somewhat more rapidly than its saturated analogue, and a  $\gamma\delta$ -olefinic linking appears to have but little effect on the rate of esterification.

The influence of substituents in both saturated and unsaturated acids is marked.

324. "The Influence of Three- and Four-membered Carbon Rings on the Refractive and Dispersive Power of Organic Compounds." By GUSTAF JIM OSTLING.

The molecular refraction and dispersion of several derivatives of cyclopropane and cyclobutane have been determined and calculated according to the formula:—

$$\text{MR} = \frac{n^2 - 1}{n^2 + 2} \times \frac{M}{L}.$$

The cyclopropane derivatives were tanacetone and its derivatives, esters of carbonic acids, a new hydrocarbon, namely, 1:2-dimethylcyclopropane, and some others. The cyclobutane compounds were chiefly esters of various acids.

It was shown that (1) the three- as well as the four-carbon ring exerts an influence on the molecular refraction. The increment in the case of a three-carbon ring is for  $M_a + 0.67$  and for  $M_D + 0.71$ ; in the case of a four-carbon ring for  $M_a + 0.45$  and for  $M_D + 0.48$ . (2) A small exaltation is noticeable when the three-carbon ring is conjugated with a double bond ( $E_{SD} = +0.2$ ). (3) The three- and the four-carbon rings have practically no influence on the molecular dispersion. (4) The conjugation of a three-carbon ring and a double bond increases the molecular dispersion about 10 per cent.

The magnetic rotation for a saturated tricyclic terpene,  $\beta$ -pinolene, has also been determined.

325. "Contributions to our Knowledge of Semicarbazones." (Preliminary Note). By ISIDOR MORRIS HEILBRON and FORSYTH JAMES WILSON.

In the course of some recent experiments the authors observed that *m*-nitrobenzylidenedeoxybenzoin on treatment with semicarbazide acetate formed two distinct semicarbazones, a colourless and a yellow modification. The addition of sodium hydroxide solution to an alcoholic solution of either the colourless or the yellow form produced an intense yellow coloration, which was destroyed by acids.

As semicarbazones have not as yet been very fully studied, the authors are extending their observations to semicarbazones derived from both saturated and unsaturated ketones and aldehydes.

Phenyl styryl ketone gives on direct treatment with semicarbazide acetate two distinct semicarbazones: a colourless form, melting at  $168^\circ$ , which is rapidly precipitated from a dilute alcoholic solution, and a more soluble yellow form obtained by dilution of the mother-liquors. On attempting to re-crystallise this yellow modification from chloroform, the authors found that it passes into a third modification which crystallises in colourless silky needles melting at  $180^\circ$ . This semicarbazone in the dry state is unstable, being gradually re-converted on exposure to diffused sunlight into the yellow modification. No melting-point for this yellow form can be obtained, as it passes when heated above  $160^\circ$  into the colourless modification melting at  $180^\circ$ . Alcoholic solutions of both colourless semicarbazones give with sodium hydroxide intensely yellow products, which are still under investigation.

The absorption spectra of these various semicarbazones are being investigated in the hope of throwing further light on the subject.

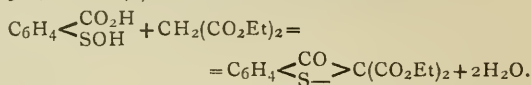
It has also been found that semicarbazones of both saturated and unsaturated aldehydes and ketones are affected by ultra-violet light, stereoisomerides being apparently produced in some cases, decomposition products in others. Investigations in this direction are also in progress.

326. "Conductivity and Dissociation of Diacetyl tartaric Acid." By STELLA DEAKIN and ALBERT CHERBURY DAVID RIVETT.

Diacetyl tartaric anhydride is hydrated too rapidly for the course of the action to be followed by the conductivity method (compare Rivett and Sidgwick, *Trans.*, 1910, xciii., 732, 1677). Since some connection appears to exist in such a case between rate of hydration and first dissociation constant of the acid, a determination of the latter was desirable, and has been made, giving the value  $2.5 \times 10^{-2}$ , a higher figure than is given by the acid corresponding with any anhydride the rate of hydration of which has been measured. The second dissociation constant approximates to  $0.11 \times 10^{-2}$ .

327. "A Synthesis of 'Thioindigo.'" (Preliminary Note). By WILLIAM GEORGE PRESCOTT and SAMUEL SMILES.

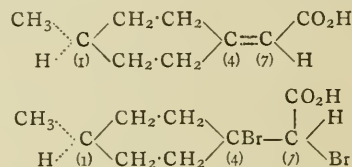
When *o*-thiol- or *o*-dithio-benzoic acid is treated with malonic acid or its ester in the presence of warm concentrated sulphuric acid a vigorous reaction occurs, and "thioindigo" is formed. From preliminary experiments the yield of the latter substance appears to be as high as about 85 per cent of the theoretical, exclusive of thioindigosulphonic acid which is simultaneously produced. Traces of hydroxybenzothioiophen were also isolated. There is no doubt that the preliminary stage of the interaction depends on the formation of the sulphylic acid (*Trans.*, 1911, xcix., 640), which then reacts as follows:—



Condensation of these thio-acids with ethyl acetate, substituted malonic acids, and similar substances may also be effected; these interactions are now being more closely investigated.

328. "Asymmetry in the supposed Absence of an Asymmetric Atom." By JAMES ERNEST MARSH.

Everest's paper (*Proc. Chem. Soc.*, xxvii., 285) disposes effectively of the claim that a new type of asymmetry exists which is not dependent on the presence of an asymmetric atom in the molecule. At the same time, the views of Everest involve him in a difficulty of another kind; in the conversion of the unsaturated acid into its dibromide, the asymmetric carbon atom (1) is represented as losing its asymmetry, while a new asymmetry carbon atom (7) is created in a different part of the molecule outside the ring:—



Perkin, Pope, and Wallach, in stating (*Proc.* 1909, xxv., 83) that the constitutional formula of the unsaturated acid "comprises no atom which can be described as asymmetric, no matter which definition of an asymmetric atom be adopted," have overlooked the definition given by the author (*Phil. Mag.*, 1888, [5], xxvi., 426). He there defined an asymmetric carbon atom as one which, when replaced by its image, gives a formula different from the original formula. This idea involved the consideration of an atom isolated from the rest of the molecule, and was justified in view of van't Hoff's theory ("Dix Années," &c., 1887, pp. 27 and 28) that the tetrahedron the centre of which is occupied by the carbon atom acquires an asymmetric form owing to the effect of four different affinities on it; thus the asymmetrically deformed atom can be considered apart from the particular groups to which it is attached. The groups may be four or less, according as the atom is situated in open-chain or in one or more rings. The atom being asymmetric will have a non-superposable image. The replacement of the atom by its image was represented in the author's paper as brought about by an exchange of position of two of the groups attached to the atom. The same inversion may be done by flying the tetrahedron (that is, by turning it inside out), a process applicable to the stereocentric benzene formulae, and one which affords a simple explanation of the phenomenon called the Walden inversion. In this method of treatment there is no need for a kind of dissection of a formula, as employed by Everest to prove four different groups, a process which must become difficult when there are several asymmetric atoms in the molecule. The views expressed in the author's paper lead to the conclusion that the methylcyclohexylidenecetic acid has three asymmetric carbon atoms in the molecule (1), (4), and (7), and that all three remain asymmetric in the bromine additive compound.



The exchange of position of any two groups or linkings attached to C (1) in either acid gives a formula different from the original one, being, in fact, that of the optical isomeride. The case is the same with C (4) and C (7). The unsaturated acid is certainly a compound of a novel type, in that with three asymmetric carbon atoms there are only two possible isomerides, and those enantiomorphous.

A somewhat similar example of a limited isomerism is that of the trihydroxyglutaric acids, where also with three asymmetric carbon atoms there are only two isomerides which are here optically inactive (without including the active forms which have only two asymmetric atoms).

Perkin and Pope (*Trans.*, 1911, xcix., 1510) claim that in the methylcyclohexylidenecetic acid "the optical activity is due to the enantiomorphous configuration of the molecule as a whole." This is certainly true, not only of this acid, but of every optically active substance whatever, and the author stated it in the paper already mentioned. The converse has also proved true that unless the molecule as a whole is asymmetric it will be optically inactive, however many asymmetric atoms it may contain. The term "centrosymmetry" is therefore not only unnecessary, but misleading; and van't Hoff's original proposition with regard to carbon still holds good, that every optically active compound has an asymmetric atom in the molecule, although the presence of asymmetric carbon does not necessarily involve optical activity.

329. "Latent Heats of Vaporisation of Mixed Liquids." (Part II.). By DAN TYRER.

In continuation of previous investigations (*Trans.*, 1911, xcix., 1633) it was pointed out that a mixture of two liquids has really two latent heats, namely:—1. Heat absorbed when 1 grm. of the mixture vaporises at constant temperature and pressure from an infinitely large quantity of the mixture of known composition. It is supposed that no change in the composition occurs in this process. 2. Heat absorbed when 1 grm. of a mixture is completely vaporised at constant temperature. If  $x$  is the composition of the liquid in (1) and  $y$  the composition of the vapour which leaves it, and if  $y$  is also the composition of the 1 grm. of liquid in (2), then it can be easily shown that—

$$(Lp)x = (Lc)y + H,$$

where  $Lp$  and  $Lc$  are the two latent heats respectively defined above, and  $H$  is the heat developed when 1 grm. of the mixture of composition  $y$  is added to an infinitely large quantity of the liquid of composition  $x$ . Values of  $Lp$  for several mixtures have been experimentally determined, and also the compositions  $y$  of the vapour boiling off from mixtures of known compositions, and from this data values of  $Lc$  have been calculated. It was shown that whilst the results for  $Lp$  do not appear to bear any simple relation to the compositions of the mixtures, those for  $Lc$  follow Trouton's equation—

$$LcM/T = \text{constant},$$

where  $M$  is the mean molecular weight of the mixture and  $T$  is the temperature.

330. "Influence of Double Linking on Optical Activity." By PERCY FARADAY FRANKLAND and HUGH HENRY O'SULLIVAN.

The authors have compared the relative rotatory effects of the allyl and  $n$ -propyl groups in the following pairs of compounds:—

|                                    | In liquid state.<br>[M] <sub>D</sub> 20°. |
|------------------------------------|-------------------------------------------|
| Menthoxyacetic allylamide .. ..    | -192.5°                                   |
| Menthoxyacetic $n$ -propylamide .. | 193.7                                     |
| Allyl menthoxyacetate .. ..        | 234.4                                     |
| $n$ -Propyl menthoxyacetate .. ..  | 234.1                                     |
| Menthyl allylaminoacetate .. ..    | 160.5                                     |
| Menthyl $n$ -propylaminoacetate .. | 158.3                                     |

The differences in molecular rotation are thus very small; indeed, in the case of the allyl and propyl menth-

oxyacetates the allyl has slightly the higher rotation at low temperatures and the propyl compound at higher temperatures.

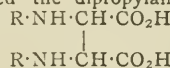
In the case of the allyl- and propyl-amides of tartaric and malic acids previously investigated by one of the authors (*Trans.*, 1906, lxxxix., 1854 and 1861), the differences in rotation were much more pronounced, and in both instances the propyl compound had the higher rotation, thus:—

|                     | In pyridine solution.            |                               |
|---------------------|----------------------------------|-------------------------------|
|                     | [M] <sub>D</sub> 20° (tartaric). | [M] <sub>D</sub> 20° (malic). |
| Allylamide ..       | +251°                            | -72.7°                        |
| $n$ -Propylamide .. | +289                             | -90.5                         |

These greater differences in rotation in the case of the tartaric and malic compounds are probably due to there only being three intervening atoms between the unsaturated and the asymmetric carbon atoms, whilst in the above menthyl compounds there are in all cases five intervening atoms between the unsaturated carbon atom of the allyl and the nearest asymmetric carbon of the menthyl group.

331. "The Action of Aliphatic Amines on  $s$ -Dibromosuccinic Acid." (Part I.). By EDWARD PERCY FRANKLAND and HENRY EDGAR SMITH.

The authors have prepared the dipropylamino- and dibutylaminosuccinic acids,



by the action of  $n$ -propylamine and  $n$ -butylamine respectively on  $s$ -dibromosuccinic acid in alcoholic solution. The reaction appears to proceed in a manner analogous to that described by E. P. Frankland (*Trans.*, 1911, xcix., 1775) in the case of benzylamine and  $s$ -dibromosuccinic acid. The alkyl-amino-acids yield copper salts, hydrochlorides, and dinitroso-derivatives.

332. "The Velocity of the Reaction between Iodic and Sulphurous Acids in various Media." By THOMAS STEWART PATTERSON and WILLIAM COLLINS FORSYTH.

The influence of methyl alcohol, ethyl alcohol,  $n$ -propyl alcohol, and of acetone on the velocity of the reaction between iodic acid and sulphurous acid was described.

## NOTICES OF BOOKS.

*Laboratorienbuch für die Anorganische Grossindustrie.* ("Laboratory Book for the Inorganic Major Industries"). By Dr. C. v. HOHORST. Halle-a.-S.: Wilhelm Knapp. 1911. (5.60 Mk.).

THIS laboratory manual is intended more particularly for the guidance of chemists who are entering upon their professional life after a course of training in chemical technology, during which they have gained a certain amount of proficiency in the usual analytical operations, and have in addition made a special study of some particular branch. It not infrequently happens that they find the equipment of the works laboratory very different from that of the laboratory belonging to the technical college, and a considerable amount of time and energy is often wasted in getting used to the altered conditions of work. The book is not to be regarded as a concise survey of all the methods which have been suggested for analysing the substances dealt with, but rather as a guide to those which, having the greatest claims to accuracy, rapidity, and simplicity, are practically universally adopted. It gives succinct directions without any superfluous detail for the carrying out of the analyses of fuels, boiler waters, and the raw material and finished products of the acid, salt, chlorine, and ammonium industries. All the tables used in these processes are included, and a chapter on the analysis of artificial manures by Dr. M. Rosenberg has been added.

We have received the following annual publications from ADAM and CHARLES BLACK, of Soho Square, London, W. :

"Who's Who" contains 2364 pages and 24,000 Biographies. Under the motto of "Honi Soit qui mal y pense" is given all that can be publicly known of the prominent men and women of the day. The present issue is carried up to the last day of August, 1911. Price—Cloth, 10s. net; limp leather, 12s. 6d.

*Who's Who Year Book* by the same publishers, is intended chiefly as a supplement to the larger volume, and is, in fact, made up of the tables formerly in that book itself. In addition will be found some original tables not to be met with elsewhere, such as Race Meetings, London Theatres with their Lessees and Managers, Professors of Universities, &c. Price 1s. net.

*The Writer's and Artist's Year Book*.—This book has been devised to meet the needs of authors and contributors to journals to enable them to decide where to place their stories and articles. The book is written for those who wish to make money by their writing, and in most cases some indication is given of the fees paid by publishers for contributions.

*The Englishwoman's Year Book and Directory*.—The work is divided into two parts. The first treats of Education, Professions, and Social Life; and the second Philanthropic effort. It is edited by G. E. Mitton, with the assistance of an Honorary Committee of prominent women of the day, and contains a mass of valuable information relative to women's professions, trades, sports, pastimes, and philanthropies. Special attention has been given to the position of women in Municipal, Industrial, and Social Life. The book can be studied with profit by every woman. Red cloth, 400 pages, price 2s. 6d. net.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. cliii., No. 22, November 27, 1911.

**$\beta$ -Rays of Radium Family.**—J. Danysz.—The author has already shown that from a tube containing radium emanation at least seven bundles of  $\beta$ -rays escape, of different and perfectly definite velocities. He has now measured these velocities, and has proved the existence of twenty-three bundles of rays; these transport very different electric charges.

**Condensation of Acid Amines in presence of Glycerin.**—L. C. Maillard.—When a mixture of glycocoll with four or five times its weight of glycerin is kept for some hours at 170°, most of the glycocoll is transformed into cycloglycylglycine. As an intermediate product the tetrapeptide triglycylglycine is formed. By a secondary reaction triglycylglycine yields the hexapeptide, pentaglycylglycine. The reaction is general, and can be applied in the synthesis of mixed cycloglycylglycines. Probably a glyceric ether is first formed, and is then destroyed with regeneration of the alcohol; thus the reaction is a generalisation of that of Th. Curtius.

*Berichte der Deutschen Chemischen Gesellschaft.*  
Vol. xlv., No. 16, 1911.

**Bismuthides and Compounds of Metals with One Another.**—A. C. Vournasos.—When bismuth and a metal are melted separately under paraffin, and one liquid is poured into the other, a crystalline precipitate is obtained. If sodium is used the precipitate is  $\text{Na}_3\text{Bi}$ ; it is insoluble in excess of sodium at the temperature of boiling paraffin,

and does not melt until a much higher temperature is reached. It is the most stable of all the bismuth-sodium compounds. It is soluble in excess of liquid bismuth, and causes a lowering of the melting-point when it dissolves; the maximum is reached with a melt of composition  $\text{Na}_3\text{Bi} + 5\text{Bi}$ . The author has applied the same method to many other elements which have a melting-point below the boiling-point of paraffin. These include K, Na, Rb, Cs, Li, Cd, Hg, Ga, In, Tl, Sn, Pb, Bi, and the metalloids P, Se, Te. The bismuthides of the alkali metals are readily oxidised in air, being converted into a black powder which consists of the alkali and bismuth suboxide. They are decomposed by water. With hydrogen they yield metallic hydrides.

*Zeitschrift für Anorganische Chemie.*  
Vol. lxxii., No. 4, 1911.

**Tantalum and Niobium Pentafluorides.**—Otto Ruff and Emil Schiller.—Large quantities of the pentafluorides of tantalum and niobium can be prepared by the action of anhydrous hydrofluoric acid on the pentachlorides, which may be obtained by heating the oxides in a current of chlorine and carbon tetrachloride. Tantalum pentafluoride forms colourless double refracting crystals of melting-point 96·8°. It is, generally speaking, stable towards non-metals, but is attacked by metals. With water it yields the pentoxide. The melting-point of niobium pentafluoride is 75·5°. In its reactions it resembles the tantalum salt, but it does not react so readily. Niobic and tantalalic acids can be separated by dissolving in hydrofluoric acid, adding excess of KI, and subjecting the mixture to fractional crystallisation. To separate tantalalic and niobic acids from titanic acid Knop's method is the best; i.e., the conversion of the oxides into chlorides and the fractional sublimation of the latter *in vacuo*.

**Decomposition of Alkali Double Sulphates of Cerium Earths by Fusion with Carbon.**—Philip E. Browning and Philip L. Blumenthal.—When the double sulphates of the alkalis and the cerium earths are fused with wood charcoal, they are readily decomposed, and are converted into a form which dissolves in hydrochloric acid with the formation of soluble chlorides. The reduction of the double sulphates to sulphides by carbon is not complete although the product is readily attacked by hydrochloric acid.

## MEETINGS FOR THE WEEK.

MONDAY, 8th.—Society of Chemical Industry, 8. "Production of Formic and Acetic Acids by the Atmospheric Oxidation of Turpentine," by C. T. Kingzett and R. C. Woodcock. "Rapid Volumetric Method for the Determination of Free Sulphur," by C. Davis and J. L. Foucar. "Relative Adsorption of Dyes by Sand and Natural Fibres," by W. P. Dreaper and W. A. Davis. "Ingrain Dyeing—Influence of certain Groups on the Re-solution Factor," by W. P. Dreaper.

TUESDAY, 9th.—Royal Institution, 3. (Christmas Lectures, adapted to a Juvenile Auditory). "The Childhood of Animals," by P. Chalmers Mitchell, LL.D., D.Sc., F.R.S.

— Society of Dyers and Colourists, 8. "Some Problems in Garment Dyeing," by F. G. Newbury. "Aluminium in the Service of Chemical Industry," by R. Seligman.

WEDNESDAY, 10th.—Royal Society of Arts, 5. (Juvenile Lectures). "Soap Bubbles," by Prof. C. V. Boys, F.R.S.

THURSDAY, 11th.—Royal Society. "Propagation of Waves through a Stratified Medium, with Special Reference to the Question of Reflection," by Lord Rayleigh. "Variation of the Specific Heat of Water, with Experiments by a New Method," by H. L. Callendar. "Mechanism of the Semi-permeable Membrane, and a New Method of Determining Osmotic Pressure," by F. T. Trouton. "Mobility of the Positive and Negative Ions in Gases at High Pressures," by A. L. Kovarik. "A New Method of Determining the Radiation Constant," by G. A. Shakespear. "Mechanics of the Water Molecule," by R. A. Houston.



# THE CHEMICAL NEWS.

VOL. CV., No. 2720.

## NOTE ON TWO THERMO-REGULATORS.\*

By W. R. BOUSFIELD, M.A., K.C.

THE first Fig. represents a regulator specially designed for an air thermostat, in which a battery of standard cadmium cells was kept. The principle is equally available for a

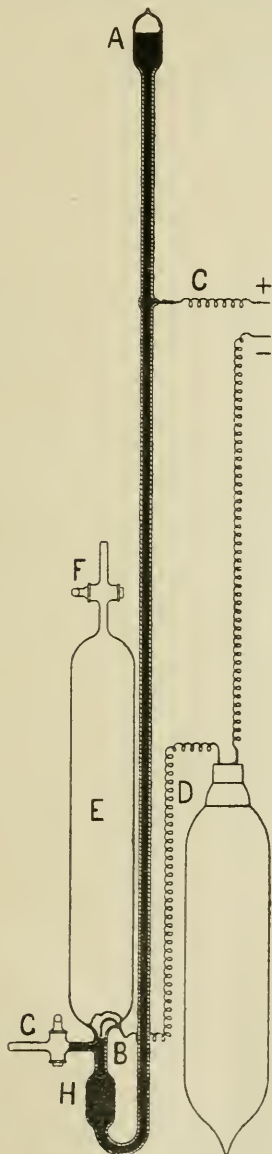


FIG. 1.

water thermostat, though slight changes of detail would be necessary.

The source of heat to be regulated was an electric radiator, worked direct from the power mains carrying an alternating current at 240 volts. *AB* are the upper and lower surfaces of a column of mercury contained in a barometer tube. Part of this mercury column is in series with the radiators and the current from the main, which passes into and out of the mercury by platinum wires, 1 mm. thick, sealed in the glass walls of the tube. The current enters through the wire *c*, which is placed sufficiently far below the surface *A* to be always immersed. The circuit is closed by contact between the lower platinum wire *d* and the lower surface *B* of the mercury. The barometer tube communicates with the bulb *E*, which is filled with hydrogen through a cock, *F*. A cock, *Cπ*, serves to regulate the quantity of mercury for the desired temperature, and enables the bulb *E* to be thoroughly washed out with hydrogen gas. Overheating of the thermostat expands the gas, and causes the mercury surface, *B*, to be

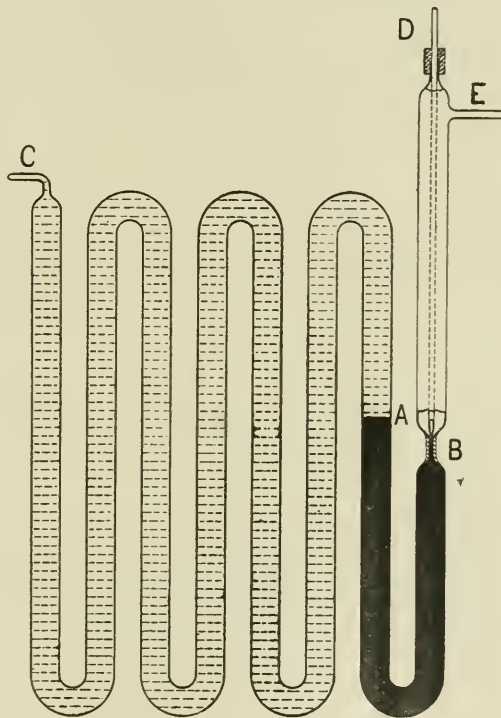


FIG. 2.

forced away from the platinum wire, thus cutting off the current. The reverse process takes place when the temperature falls below the mean.

The tube is furnished with two bulbs at *A* and *H*. The mean pressure in *E* must be so chosen that the mercury in *A* normally occupies about half the bulb *A*. The purpose of the bulb *H* is to supply sufficient mercury to fill the bulb *A* in case of overheating, without allowing the lower level of the mercury to be depressed to the bottom of the tube, which would permit air-bubbles to pass and spoil the vacuum in *A*.

It is best to instal the regulator with the mean pressure in *E* about equal to mean atmospheric pressure. The length of the tube will then be that of an ordinary barometer. In this way the possible leakage of the mobile hydrogen through defective taps is prevented.

In such an apparatus, where the full current through the radiators from a pressure of 240 volts in the mains passes through the mercury, and gives rise to a spark at *B* on breaking the contact, it was a matter of vital importance to

\* Exhibited before the Faraday Society, December 6, 1911.



prevent oxidation or other deterioration of the surface of the mercury. For instance, it was anticipated that nitrogen with traces of oxygen and water vapour might give rise to nitric acid and cause trouble. Hydrogen forms no compound with mercury, and was tried in the first instance. It proved completely successful. Last winter the regulator was kept working day and night for six months, maintaining a temperature of about 18° C. No tarnishing of the mercury surface has taken place, and it seems as bright as when it was first installed.

A point of importance is that the regulation is independent of variations of atmospheric pressure, owing to the gas being completely enclosed and working against a vacuum.

To find the sensitiveness, let—

P = pressure of hydrogen in mm. of mercury.

V = volume in cc.

$\theta$  = absolute temperature.

A = sectional area of tube at A in cm<sup>2</sup>.

B = sectional area of tube at B.

$x$  = distance of mercury surface at B, below platinum-point in mm.

$h$  = mean height of mercury level at A, above platinum-point in mm.

$$P = h + \left(\frac{B}{A} + 1\right)x$$

$$\delta P = \left(\frac{B}{A} + 1\right)\delta x$$

$$\delta V = B\delta x \times \frac{1}{10} \text{ (since } x \text{ is mm.)}$$

$$PV = C\theta$$

$$C \frac{d\theta}{dx} = P \frac{dV}{dx} + V \frac{dP}{dx}$$

$$= \frac{1}{10} B P \cdot \left(\frac{B}{A} + 1\right)V$$

$$\text{i.e.,—} \quad \frac{1}{\theta} \cdot \frac{d\theta}{dx} = \frac{B}{10V} + \frac{1}{P} \left(\frac{B}{A} + 1\right).$$

For greatest sensitiveness  $\frac{d\theta}{dx}$  must be as small as possible. Hence, V and A must be as large as possible. The sensitiveness is also increased by making P large, but for the reasons mentioned it is best kept at about atmospheric pressure.

If—

$$B = 0.1 \text{ cm}^2. A = \text{cm}^2.$$

$$P = 760 \text{ mm. } V = 760 \text{ cc.}$$

$$\theta = 300^\circ \text{ equivalent to } 27^\circ \text{ C.}$$

we have—

$$\frac{d\theta}{dx} = \frac{300}{760} (0.01 + 1.025)$$

$$\delta\theta = 0.4 \delta x.$$

With these dimensions 1 mm. fall of the mercury contact surface at B corresponds to 0.4° C., or 0.01° C. to one-fortieth of a mm.

The sensitiveness realised depends of course upon the activity of stirring of the contents of the thermostat. The comparative sensitiveness relative to that of a regulator depending on this expansion of mercury or toluene is chiefly influenced by the fact of the small heat capacity of the hydrogen contained in the bulb and the large surface available for rapid heat exchange.

*Water-bath Regulators.*—This is a modified form of Lowry gas regulator. It was designed in the form of a grid, so as to be placed near the side of a large water-bath, in order to take up as little room as possible. The last U-shaped limb, Fig. 2, contains mercury from B to A. The remainder, from A to C, is filled with toluene. Easy

filling is secured by the use of a small tube c, which is sealed with a blowpipe when the mercury and toluene are in place. It is not difficult to fuse the tube c when filled with toluene, as the heating causes the toluene to boil near c and fill the tube with vapour, which excludes air, so that when the tube cools it is filled with toluene right up to the end without an air-bubble. D is the gas inlet pipe, which is closed by the expansion of the mercury. E is the gas outlet pipe. The tube D is kept in place by a rubber stopper, which permits of its ready removal. Regulation to any desired temperature is easy. The regulator is placed in the bath, which is kept at the desired temperature for a few minutes. The tube D is removed, and an excess of mercury poured in. When the temperature is as desired, the excess of mercury is sucked out with a filter-pump through the tube D. Thus the right quantity of mercury is obtained corresponding to the required temperature. This form of regulator is affected by variations of gas and atmospheric pressure. It is not difficult to secure regulation of the thermostat within  $\pm 0.01^\circ \text{ C.}$

## VOLUMETRIC DETERMINATION OF MERCURY.

By CARL E. SMITH.

ABSTRACTS of a report by a Committee of the Division of Pharmaceutical Chemistry of the American Chemical Society have appeared in recent journals (see *American Journal of Pharmacy*, 1911, lxxiii., 186), the work reported on being a comparison of various methods for the determination of mercury in the medicinal compounds of this metal.

The purpose of these notes is to relate some recent experiences with two of these methods, which are probably the simplest and most reliable of those mentioned in the report, the Hempel method for mercurous and the Rupp method for mercuric compounds. It is desired also to call attention to one other, which is perhaps the best volumetric method available for some purposes.

The writer's experience with the Hempel method, in its application to calomel and mercurous iodide, corroborates to a considerable extent the results of the committee. The objectionable feature of it, noted by several of the members, that long-continued shaking is needed to bring the salt into solution, may be eliminated, it was found, by the simple change of adding the iodine solution first, instead of the potassium iodide. When this is done and the mixture at once shaken vigorously in a stoppered flask, solution is effected very quickly. The final result is the same in either case, as comparative trials have shown. It seems advisable, also, to increase the quantity of sample, to lessen the experimental error, in the case of calomel to about 1 grm. The most satisfactory results were obtained when working in the following manner:—To about 1 grm. of calomel, accurately weighed, contained in a glass-stoppered 300 cc. Erlenmeyer flask, add 50 cc. of N/10 iodine solution. Mix by rotating until the salt is thoroughly moistened, then add a solution of 2 grms. of potassium iodide in 10 cc. of water, and at once shake the stoppered flask vigorously until solution is complete. Titrate the excess of iodine with N/10 sodium thiosulphate, using starch solution as indicator, adding the latter when the liquid is nearly decolorised. Each cc. of N/10 iodine solution consumed corresponds to 0.02355 grm. of mercurous chloride.

A sample of calomel, practically chemically pure, assayed by this method 99.5 to 100.0 per cent, the average of six determinations being 99.7 per cent, with some variation in the working details. Practically the same figures were obtained with yellow mercurous iodide containing slight traces of impurities.

The criticism of the Rupp method, that reduction of the mercury is not complete within a reasonable time without the use of heat, and that, when heat is employed, the

mercury is not easily dissolved afterwards, is well founded, if Rupp's directions in outlining the method (*Berichte*, 1906, xxxix., 3702) be taken literally as regards the quantity of alkali to be used. While his directions lead to the inference that only enough is required to combine with the acids formed by the reaction, his figures in the same paper show that he used a decided excess, not less than 10 cc. of normal solution for 0.2 gm. of mercuric chloride. The divergent opinions regarding this method by the members of the committee are doubtless due chiefly to differences in the quantities of alkali used. When the above mentioned proportions are taken the reaction is almost instantaneous, unless the solution is excessively diluted, and may safely be regarded as complete within five minutes, without heating. It will do no harm to use a still larger excess of alkali or to let the mixture stand longer. Shaken in a stoppered flask with the iodine solution, the precipitate is then dissolved very readily. A large excess of acetic acid is to be avoided, as it tends to make the result too low, which is also the experience of Mr. L. D. Havenhill of the committee. The best results were obtained by carrying out the details as follows:—Dissolve about 0.5 gm. of powdered mercuric chloride, accurately weighed, contained in a glass stoppered 300 cc. Erlenmeyer flask, in a solution of 2 grms. of potassium iodide in 10 cc. of water. Add 25 cc. of normal caustic alkali solution and 6 cc. of 40 per cent formaldehyde solution. Mix by swirling the flask occasionally during ten minutes, then acidulate with about 5 cc. of 36 per cent acetic acid. Add 50 cc. of N/10 iodine solution and shake vigorously in the stoppered flask until the mercury is dissolved. Titrate the excess of iodine with N/10 sodium thiosulphate solution, adding starch solution when the liquid is nearly decolorised. Each cc. of N/10 iodine solution corresponds to 0.01355 gm. of mercuric chloride.

Chemically pure mercuric chloride gave by this method 99.8 to 100.3 per cent, with an average of 100.1 per cent in five determinations. Similar results were obtained with mercuric iodide, oxide, ammoniated mercury, and mixtures of mercuric chloride and ammonium chloride coloured with aniline dyes. It is the official method of the German Pharmacopœia, 5th revision, 1910, for the assay of mercuric chloride tablets and ointment of ammoniated mercury.

The third method alluded to above consists in the titration of mercuric compounds, in nitric acid solution, with sulphocyanate in exactly the same way as the titration of silver. It is not applicable in presence of chlorides, and probably not in presence of other halogens. It was first made serviceable for accurate work by R. Cohn (*Ber.*, 1901, xxxiv., 3502) and simplified by Rupp and Kraus (*Ibid.*, 1902, xxxv., 2015). For illustrations of its application see below. The writer has no personal experience with this method, but his associates have found it accurate and useful for the assay of technical mercuric oxide containing iron. The German Pharmacopœia uses it for the assay of several galenic preparations. For the convenience of any readers of this journal interested in the subject who may not have access to this book, the assay methods for mercury preparations prescribed therein are given here:—

**Mercuric Chloride Tablets.**—Composed of equal parts of mercuric chloride and sodium chloride, coloured with aniline dye. Dissolve two tablets of about 1 gm. each, accurately weighed, in water and dilute to 100 cc. In 20 cc. of the solution dissolve 1 gm. of potassium iodide, add 10 cc. of a 15 per cent solution of potassium hydrate and 3 cc. of a 40 per cent solution of formaldehyde with 10 cc. of water. After one minute add 25 cc. of 30 per cent acetic acid, 25 cc. of N/10 iodine solution, and shake until the mercury is dissolved. Titrate the excess of iodine with N/10 sodium thiosulphate solution, using starch solution as indicator. Each cc. of N/10 iodine solution consumed corresponds to 0.01355 gm. of mercuric chloride.

**Ointment of Ammoniated Mercury.**—Consists of 10 per cent of ammoniated mercury and white vaseline. Heat about 5 grms. of the ointment, accurately weighed, in a

small flask with 25 cc. of 12.5 per cent hydrochloric acid on a water-bath. Mix frequently by rotating the flask during ten minutes. Pour the acid liquid into a 100 cc. flask, rinse the vaseline and flask repeatedly with water, and dilute the combined liquid and washings to 100 cc. Transfer 25 cc. to a glass-stoppered flask, add 1 gm. of potassium iodide, and proceed further as directed for the assay of mercuric chloride tablets. Each cc. of N/10 iodine solution consumed corresponds to 0.01257 gm., approximately, of ammoniated mercury.

**Mercuric Salicylate.**—Contains about 55 per cent of mercury. Dissolve about 0.3 gm. of the salt, accurately weighed, in dilute sodium hydrate solution, acidulate with acetic acid, and add 25 cc. of N/10 iodine solution. Let the mixture stand in a closed flask for three hours at room temperature, rotating it occasionally. Titrate the excess of iodine with N/10 sodium thiosulphate solution. Each cc. of N/10 iodine solution consumed corresponds to 0.0100 gm. of mercury.

**Mercury Plaster.**—Contains 20 per cent of mercury; made with lead plaster, wool fat, and yellow wax. Heat about 3 grms. of the plaster mass, accurately weighed, with 20 cc. of nitric acid, sp. gr. 1.38 to 1.40, in a flask having a wide neck and connected with a reflux condenser. Heat about ten minutes, or until mercury globules are no longer visible in the sandy deposit of lead nitrate, add 25 cc. of water, and heat again until the fat has separated, leaving the aqueous layer clear. Cool and pour the solution through a tuft of absorbent cotton into a 100 cc. flask. Break up the disk of fat, rinse it and the flask with 4 or 5 portions of 5 cc. each of water, and to the combined liquids add potassium permanganate until permanently red or until brown flakes separate. Decolorise or clarify the solution by addition of ferrous sulphate solution and dilute to 100 cc. To 25 cc. of the solution add 2 cc. of a 10 per cent solution of ferric alum, and titrate with N/10 ammonium sulphocyanate. Each cc. consumed corresponds to 0.0100 gm. of mercury.

**Mercury Ointment.**—Contains 30 per cent of mercury; made with wool fat, pea nut oil, lard, and mutton tallow. Proceed as directed for the assay of mercury plaster, using about 2 grms. of the ointment and 20 cc. of nitric acid.

**Ointment of Red Mercuric Oxide.**—Contains 10 per cent of mercuric oxide; made with white vaseline. Proceed as directed for the assay of mercury plaster, using about 5 grms. of the ointment and 20 cc. of nitric acid. Continue heating until the red colour of the mercuric oxide has disappeared. Each cc. of N/10 ammonium sulphocyanate solution corresponds to 0.0108 gm. of mercuric oxide.

The factors given throughout these notes are based on the atomic weights having  $O=16$  as the standard. If the volumetric solutions used are made by the  $H=1$  standard, either the factors or the final results should be multiplied by 0.992.—*American Journal of Pharmacy*.

## CHEMICAL NATURE OF SOIL ORGANIC MATTER.\*

By OSWALD SCHREINER and EDMUND C. SHOREY.

(Continued from p. 7).

### PARAFFIN HYDROCARBONS.

The paraffin hydrocarbons represent the simplest form of organic compounds and are widely distributed in nature. The lowest member of this group, methane or marsh gas ( $CH_4$ ), is a constant product of the decomposition of organic matter under certain conditions. Higher members of the group, liquid and solid, occur as mixtures very widely distributed in the earth's crust as petroleum,

\* Bulletin No. 74, U.S. Department of Agriculture, Bureau of Soils.



asphalt, or similar deposits and also in mineral resins. The occurrence of paraffin hydrocarbons in plants is not very common, and so far as observed is confined to a few members of the group and to a few species of plants. The large deposits in the earth's crust can not, then, be attributed to the accumulation of unchanged plant residues, and a great many theories have been propounded to account for these deposits, most of them based on some transformation of organic material.

In spite of the fact that these hydrocarbons are of rather rare occurrence in plants and are seldom added to soil in plant *débris*, the wide distribution of extensive deposits of such compounds and the occurrence also of mineral resins and shales from which hydrocarbons can be obtained in the rocks from which soils are formed might lead one to expect to find some trace of these compounds in the soil. The question is also raised by this consideration whether some of the processes by which hydrocarbons have been formed from more complex organic compounds may not take place in the soil and escape recognition because the conditions are not favourable for the accumulation of these products in the soil. The production of the simplest paraffin hydrocarbon, methane, is known to take place in soil organic matter when submerged under water, as in swamps. The production here is supposed to be due to the activity of anaerobic micro-organisms, but it is not known that absolutely anaerobic conditions are essential to this production or that methane may not be formed in small quantities in ordinary soils. Methane is present in the gases from the combustion of fuel even when excess of oxygen is available, and it has been found in the combustion of organic compounds in elementary analysis that some of the carbon may be present in the products of combustion as methane instead of carbon dioxide, and this when the combustion was carried on in pure oxygen (Dunstan, *Proc. Chem. Soc.*, 1896, xii., 48). It may be, therefore, that in the decomposition of organic matter the formation of methane rather than carbon dioxide depends on the structure or constitution of a portion of the material decomposed, and similarly more complex members of this series may also be formed.

In connection with this discussion of hydrocarbons in soils it should be noted that there are in nearly all soils dark coloured particles of organic matter that are very resistant to solvents and the action of either acids or alkalis. These sometimes are evidently particles of charcoal or coal that may have found their way into the soil, but a considerable portion is often made up of structureless bituminous-like material having the elementary composition so far as examined of lignites or brown coals. Whether this is formed in the soil is a matter for further investigation. Since such material often makes up a considerable portion of the organic content, its composition, constitution, and origin should be considered. One paraffin hydrocarbon has been isolated from a soil, and while in this particular case there is nothing to indicate that it may not be an unchanged plant residue, the isolation is of interest not only in accounting for a small portion of the organic matter, but also in that it opens up the question of a possible connection between the processes that go on in the soil and the processes by which paraffin hydrocarbons have been formed in nature.

#### *Hentriacontane*, $C_{31}H_{64}$ .

A peaty soil from North Carolina containing 27 per cent organic carbon when extracted with boiling 95 per cent alcohol yields a dark coloured extract, from which on cooling a light yellow micro-crystalline body separates. This material was separated by filtration and the alcohol removed from the filtrate by evaporation, the volume being kept constant by the addition of water. There was thus formed a reddish brown precipitate which after separation and washing was in the form of a brown resinous powder. Extraction of this with boiling petroleum ether yielded a light coloured solution, which after removal of the petroleum ether left a light yellow oily residue. This was saponified

with alcoholic potash, the alcohol removed, and the soap dried and extracted with petroleum ether. On evaporation of the petroleum ether the residue was a light coloured waxy mass, completely soluble in a relatively large volume of hot alcohol. On cooling the alcoholic solution so obtained, there was a separation of a feathery micro-crystalline body which was collected, washed, and purified by re-crystallising several times from alcohol.

As thus obtained, the body was a hard waxy mass, melting at  $68^{\circ} \text{C.}$ , and having a specific gravity of 0.780 at its melting-point. It was readily soluble in ether and petroleum ether, difficultly soluble in hot and very slightly soluble in cold alcohol. It was unacted on by fuming nitric acid at room temperature and did not absorb bromine.

Elementary analysis gave the following figures:—

|             | Found. | Calculated for $C_{31}H_{64}$ . |
|-------------|--------|---------------------------------|
| Carbon ..   | 84.14  | 85.32                           |
| Hydrogen .. | 15.01  | 14.68                           |

The method by which this body was obtained fixes it as either a hydrocarbon or a higher alcohol. Its behaviour toward nitric acid and its elementary composition prove that it can not be a higher alcohol, and its behaviour toward bromine shows that it must be a saturated compound. It being thus fixed as a saturated or paraffin hydrocarbon, its melting-point shows it to be hentriacontane.

Hentriacontane is a member of the paraffin series found in the paraffin residue of some petroleum. It has also been found in beeswax, together with another member of the same series, heptacosane,  $C_{27}H_{56}$  (Schwald, *Ann. Chem.*, 1886, ccxxxv., 117). It occurs also in some plants, having been found in the leaves of *Gymnema silvestre* (Power and Tutin, *Pharm. Journ.*, 1904, [4], xix., 234), in tobacco leaves (Thorpe and Holmes, *Journ. Chem. Soc.*, 1901, lxxix., 982), and in East India Ko-sam seeds (*Brucea sumatrana*) (Power and Lees, *Pharm. Journ.*, 1903, [4], xvii., 183). With this information regarding its occurrence as a natural product, and in the absence of any information regarding the possibility of its formation from other soil organic matter, this paraffin hydrocarbon may be regarded as an unchanged plant residue.

#### HYDROXY-FATTY ACIDS.

Hydroxy acids of the fatty series are very widely distributed in the vegetable kingdom. One or more of the three hydroxy acids—malic, citric, or tartaric—is usually present in an acid plant or fruit juice, and some of the less common, such as glycollic, also occur in plants. Some members of this group can be formed by micro-organisms from more complex material—lactic acid by the lactic fermentation of sugar and citric acid by citromycetes (Mazé, *Ann. Inst. Pasteur*, 1909, xxiii., 830). All members of the group, however, seem to be readily broken down by other bacteria or fungi into simpler compounds with the loss of the hydroxy character. Lactic acid goes readily to butyric and others to acetic or formic acid or formaldehyde. In view of this fact, while there is no doubt that vegetable acids of this group are added to soils in large quantities and become temporarily, at least, a part of the organic matter of the soil, it does not seem likely that they would persist unchanged for any length of time.

Two hydroxy acids of the fatty series have been isolated from soils, but neither are known as natural products. These are  $\alpha$ -hydroxystearic acid and the dihydroxystearic acid previously described (*Bull.* 53, Bureau of Soils, U.S. Dept. Agr., 1909; *Journ. Am. Chem. Soc.*, 1908, xxx., 1599). Both must be looked on at present as the products of the action of micro-organisms, probably fungi, on some of the organic matter known to be of plant or animal origin.

While at present little is known of the processes by which these compounds are formed in the soil, and little can be said that is not of a speculative nature, it may be of interest at this point to note the laboratory methods by



which hydroxy acids are formed. Three general methods are known by which the hydroxy acids are formed from the corresponding acid. These are:—Making a halogen substitution product and treating this with silver oxide and water; making an amido derivative and treating this with nitrous acid; and making a sulphonic-acid derivative and treating it with caustic potash.

In attempting to find a parallel between these reactions and the processes likely to take place in the soil, the second method seems to be the only one that offers any foundation for a theory. It is known that amido compounds result from the decomposition of more complex nitrogenous compounds and may possibly be formed or built up by the action of ammonia which is commonly formed in soils. Nitrous acid, as the result of denitrification or as the first stage in the change of ammonia into nitrates, is formed in nearly all soils and would supply the reagent required in the second stage of the reaction.

In addition to these purely chemical methods of formation, there are the biological formations by fungi or bacteria to be considered, but this would lead somewhat afield from the purposes of the present *Bulletin*.

*α-Monohydroxystearic Acid, C<sub>18</sub>H<sub>36</sub>O<sub>3</sub>.*

When the humus extract of a soil obtained by extraction with dilute alkali is acidified, a brown or black flocculent precipitate of the so-called humus bodies is formed. If this precipitate is separated by filtration, washed, and treated while still moist with boiling 95 per cent alcohol, a portion of the precipitate goes into solution. The amount of the humus precipitate so dissolved varies with the character of the soil treated, but the alcoholic solution obtained in this way is always dark coloured. On careful evaporation of this alcoholic solution, adding water to keep the volume constant until the alcohol is removed, there is formed a brown or reddish brown precipitate, which can be separated by filtration. When so separated, washed, and dried it is in the form of resinous lumps or powder, varying in colour, melting-point, and composition with the soil from which it was obtained.

On extracting this resinous material with petroleum ether there is obtained an extract generally colourless or light coloured, which on evaporation of the petroleum ether leaves a residue which may vary from an oily semisolid mass to a waxy solid. This residue is generally wholly soluble in hot alcohol. From this alcoholic solution there sometimes separates on cooling a white or yellowish microcrystalline mass or powder which in the case of one soil has been identified as *α*-hydroxystearic acid.

The soil from which this compound was obtained was a sample of Elkton silt loam, a type covering a considerable area in Maryland. This soil is almost white in colour, high in clay and silt, and contains 0.53 per cent organic carbon and 0.066 per cent nitrogen. The sample examined was one of several hundred pounds obtained from the Eastern Shore of Maryland.

This soil when treated with 2 per cent sodium hydroxide solution yields an extract much darker than might be expected from a soil so light in colour. From this brown alkaline extract there is precipitated on acidifying with sulphuric acid a brown flocculent mass. On separation of this by filtration, washing, and treating with boiling 95 per cent alcohol, there is obtained an alcoholic solution nearly as dark in colour as the original alkaline extract. The precipitate formed by evaporation of the alcohol and addition of water was, after filtration, washing, and drying, a brown mass easily pulverised.

Extraction of this brown powder with petroleum ether and evaporation of the solvent left an oily semisolid light yellow mass, which was completely soluble in hot 95 per cent alcohol. On cooling this alcoholic solution there separates a yellow microcrystalline powder, which after separation by filtration, washing with cold alcohol, dissolving again in hot alcohol, and repeating the separation several times, can be obtained free of colour and of constant melting-point.

The substance so obtained melts at 84–85° C., is soluble with difficulty in cold alcohol, readily in hot alcohol, cold ether, or petroleum ether. It crystallises usually in small irregular leaflets, but can be crystallised from alcohol by very slow cooling, in six-sided plates. It forms salts with alkalis soluble in water and can be obtained from such solution unchanged by acidifying and extracting with ether.

Elementary analysis of this compound gave the following figures:—

|             | Found. | Calculated for C <sub>18</sub> H <sub>36</sub> O <sub>3</sub> . |
|-------------|--------|-----------------------------------------------------------------|
| Carbon ..   | 72.09  | 72.00                                                           |
| Hydrogen .. | 12.17  | 12.00                                                           |
| Oxygen ..   | 15.84  | 16.00                                                           |

This composition corresponds with that of the monohydroxystearic acids, two of which are known, designated *α* and *β* respectively, and having the formula C<sub>18</sub>H<sub>36</sub>O<sub>3</sub>. The properties of the acid isolated from the soil fix it as the *α*-acid. The *α*-acid is much less soluble in alcohol than the *β*-acid, and the *β*-acid, moreover, forms an anhydride on heating with hydrochloric acid, which is not the case with the *α*-acid nor the acid from the soil. The melting-points of the *α*- and *β*-acids are so nearly the same that this property can not be used to distinguish between them. The melting-point of the pure *α*-acid, artificially prepared, remained unchanged on mixing with the acid from the soil, and this fact, together with the composition found and sparing solubility in alcohol and failure to form an anhydride, is sufficient to establish the identity of the acid from the soil as *α*-monohydroxystearic acid.

*α*-Hydroxystearic acid is easily made in the manner described by Sadomsky (*Ber.*, 1891, xxiv., 2388). When stearic acid is treated with red phosphorus and bromine, *α*-bromostearic acid is formed. On heating this with alcoholic potash the potassium salt of *α*-hydroxystearic acid is formed, and on acidifying the aqueous solution of this salt the acid is set free and can be extracted with ether.

*α*-Hydroxystearic acid is not known to occur in any natural animal or vegetable product, and up to the present has been isolated from only one soil.

The possible origin of this acid has already been discussed from a speculative point of view, and while it is not known as a natural product it must be remembered that natural fats and oils are usually complex mixtures of glycerides, and that the chemistry of such glycerides as occur in these products in small amounts is very incomplete. More complete chemical knowledge of the natural fats and oils may show the presence of *α*-monohydroxystearic acid. The method of its laboratory preparation does not suggest any possible parallelism in the soil as was the case when the origin of dihydroxystearic acid was under discussion.

In the earlier literature of the hydroxystearic acids there is some confusion of nomenclature, as well as disagreement regarding their constitution. The *β*-acid described by Saytzeff (*Journ. Prakt. Chem.*, 1887, [2], xxxv., 369) was designated as the *α*-acid by Geitel (*Journ. Prakt. Chem.*, 1888, [2], xxxvii., 53). The designations *α*- and *β*-acid seem to have been used primarily to distinguish isomers, the constitution of which were not known. The constitution, as now accepted and established by Shukoff and Schestakoff (*Journ. Prakt. Chem.*, 1903, [2], lxvii., 415), is not in harmony with the common meaning of *α* and *β* designations. In the simple hydroxy-fatty acids the term *α* is applied to that acid having the hydroxyl group next the carboxyl group, for example, *α*-hydroxypropionic acid (lactic) is represented thus: CH<sub>3</sub>.CHOH.COOH; the term *β* is applied to that acid having the hydroxyl on the second carbon atom, for example, *β*-hydroxypropionic (hydracrylic) is represented thus: CH<sub>2</sub>OH.CH<sub>2</sub>COOH. The constitution of the *α*- and *β*-hydroxystearic acids is represented as follows: *α*-acid, CH<sub>3</sub>(CH<sub>2</sub>)<sub>6</sub>CHOH(CH<sub>2</sub>)<sub>9</sub>COOH; *β*-acid, CH<sub>3</sub>(CH<sub>2</sub>)<sub>7</sub>CHOH(CH<sub>2</sub>)<sub>8</sub>COOH. In neither case is there *α*- or *β*-structure. The authors in discussing these formulae used the designations: 1. 11. for the *α*-acid and 1. 10.

for the  $\beta$ -acid, 1 being the carbon atom of the carboxyl group and 10 and 11 the carbon atoms counting from 1 to which the hydroxyl group was attached. Since, however, these acids are still generally described and referred to in the literature as  $\alpha$  and  $\beta$  these terms have been used in this paper with this explanation.

(To be continued)

## CHEMICAL ENERGY.\*

By J. E. MILLS.

IF 16 grms. of oxygen gas at  $0^\circ$  C. are placed in contact with 2.016 grms. of hydrogen gas at the same temperature, and both under atmospheric pressure, no reaction is evident. But if a negligible amount of heat be supplied to the mixture in the form of an electric spark, a violent reaction takes place, and 18.016 grms. of water are formed, and 68,511 calories of heat are given out (Mixer, *Am. Journ. Sci.*, 1903, [4], xvi., 214). (The value given is the mean of the values obtained by Thomsen, Schüller and Wartha, Than, and Mixer, after reduction to the calorie at  $15^\circ$  to  $16^\circ$  as the unit; Mixer thinks the value correct to one-tenth of 1 per cent). If the reaction took place at a different temperature, or under different conditions of pressure or volume, the amount of heat evolved would have been different, but the chemical reaction in each case would have been the same.

From whence came the enormous amount of heat given out by the reaction? Why and how does the amount of heat given out vary under different conditions? Why did not the reaction take place when the hydrogen and oxygen were first mixed?

It is the purpose of this paper to answer these questions and to point out certain facts concerning chemical energy, and certain possibilities regarding the relation of chemical energy to electrical and other forms of energy.

### The Source of the Energy given out by the Reaction.

If the term "absolute zero of temperature" be used, some one will object that there may be no absolute zero of temperature, that we are not certain of the existence of molecules, and that if they do exist we certainly do not know that they cease to move at the so-called absolute zero. Granting for the present the validity of the objection, we will not use the term absolute zero, but will speak of  $-273^\circ$  C. No one will deny the existence of that temperature since a temperature below  $-260^\circ$  C. has already been reached.

For reasons which will appear later, I wish to get the total amount of heat necessary to raise 2.016 grms. of hydrogen, and 16 grms. of oxygen, and 18.016 grms. of water (ice), from  $-273^\circ$  C. to  $0^\circ$  C. The measurements given in the table below enable this data to be obtained correct to within a few calories.

|                         | Hydrogen.     | Oxygen.       | Water.      |
|-------------------------|---------------|---------------|-------------|
| Melting-point..         | $-258.9$ (a)  | $-227$ (c)    | 0           |
| Boiling-point..         | $-252.59$ (a) | $-182.80$ (a) | 100         |
| Specific heat of solid  | $2.3$ (b)     | $0.25$ (b)    | $0.294$ (c) |
| Specific heat of liquid | $3.4$ (c)     | $0.347$ (e)   | 1.000       |
| Heat of fusion ..       | $16$ (c)      | —             | $79.90$ (g) |
| Heat of vaporisation    | $123.1$ (c)   | $50.97$ (e)   | —           |
| Specific heat of gas    | $3.410$ (d)   | $0.275$ (f)   | —           |

(a) Travers, Senter, and Jaquero, *Phil. Trans.*, A, 1903, cc., 170.

(b) This value was estimated by Kopp from the specific heat of its solid compounds. We know almost with certainty that the specific heat of the solid is not so great as the specific heat of the liquid, and probably the value given is nearly correct.

- (c) Dewar, *Proc. Roy. Soc.*, A, 1905, lxxvi., 325; 1902, lxxix., 361; 1904, lxxiii., 251. He determined the specific heat of ice,  $-252.6$  to  $-188 = 0.146$ ,  $-78$  to  $-188 = 0.285$ ,  $-78$  to  $-18^\circ = 0.403$ .  
 (d) Wiedemann, *Pogg. Ann.*, 1876, clvii., 1; *Phil. Mag.*, 1876, [5], ii., 81.  
 (e) Alt, *Zeit. Phys. Chem.*, 1905, li., 252; *Phys. Zeit.*, 1905, vi., 346; *Ann. der Physik.*, 1904, xiii., 1010; "Dissertation," Munchen, 1903.  
 (f) Regnault, *Mem. de l'Acad.*, 1862, xxvi., 1.  
 (g) Smith, *Phys. Rev.*, 1903, xvii., 193.

The total heat necessary to raise these substances from  $-273^\circ$  to  $0^\circ$  C. may therefore be estimated as follows:—

### Hydrogen (1 Grm.).

|                                                              | Calories.  |
|--------------------------------------------------------------|------------|
| Specific heat of solid, $-273^\circ$ to $-258.9^\circ =$     |            |
| $14.1 \times 2.3$ .. .. .                                    | $= 32.4$   |
| Latent heat of fusion .. .. .                                | $= 16$     |
| Specific heat of liquid, $-258.9^\circ$ to $-252.59^\circ =$ |            |
| $6.31 \times 3.4$ .. .. .                                    | $= 21.4$   |
| Latent heat of vaporisation .. .. .                          | $= 123.1$  |
| Specific heat of gas, $-252.59$ to $0^\circ =$               |            |
| $3.410$ .. .. .                                              | $= 861.3$  |
| Total heat, $-273^\circ$ to $0^\circ$ C. for 1 grm. ..       | $= 1054.2$ |
| Total heat, $-273^\circ$ to $0^\circ$ C. for 2.016 grms.     | $= 2125.2$ |

### Oxygen (1 Grm.).

|                                                           |            |
|-----------------------------------------------------------|------------|
| Specific heat of solid, $-273^\circ$ to $-227^\circ =$    | 46         |
| $\times 0.25$ .. .. .                                     | $= 11.50$  |
| Latent heat of fusion, estimated .. .. .                  | $= 5.70$   |
| Specific heat of liquid, $-227^\circ$ to $-182.8^\circ =$ |            |
| $44.2 \times 0.347$ .. .. .                               | $= 15.34$  |
| Latent heat of vaporisation .. .. .                       | $= 50.97$  |
| Specific heat of gas, $-182.8^\circ$ to $0^\circ =$       |            |
| $182.8 \times 0.2175$ .. .. .                             | $= 39.75$  |
| Total heat, $-273^\circ$ to $0^\circ$ C. for 1 grm. ..    | $= 123.26$ |
| Total heat, $-273^\circ$ to $0^\circ$ C. for 16 grms.     | $= 1972.2$ |

### Water (1 Grm.).

|                                                           |            |
|-----------------------------------------------------------|------------|
| Specific heat of solid, $273^\circ$ to $0^\circ$ .. .. .  | $= 80.34$  |
| Latent heat of fusion .. .. .                             | $= 79.90$  |
| Total heat, $-273^\circ$ to $0^\circ$ C. for 1 grm. ..    | $= 160.24$ |
| Total heat, $-273^\circ$ to $0^\circ$ C. for 18.016 grms. | $= 2886.9$ |

The 18.016 grms of water at  $0^\circ$  C. contain, therefore, at least 2887 calories, and since 68,511 calories of heat were given out by the reaction of the hydrogen and oxygen gases, these gases before the reaction contained at least 71,398 calories of energy. Of this total amount of energy, 2125 calories were supplied to the 2.016 grms. of hydrogen, and 1972 calories were supplied to the 16 grms. of oxygen, in converting them from the solid condition at  $-273^\circ$  C. to the gaseous condition at  $0^\circ$  C.—a total of 4097 calories. It follows therefore that while in the solid condition at  $-273^\circ$  C. the oxygen and hydrogen contained at least 71,398—4097 = 67,301 calories of energy. Now, Dewar (*Proc. Roy. Soc.*, 1904, lxxiii., 251) has shown by slight extrapolation of measurements extending to  $-258.9^\circ$  C. that the molecular volume of oxygen at  $-273^\circ$  C. is 21.21 cc., of hydrogen 24.18 cc., and of ice 19.21 cc.

Therefore the 16 grms. of oxygen and the 2.016 grms. of hydrogen together at  $-273^\circ$  C. occupy 34.78 cc., and when occupying this volume at that temperature they contain 67,300 calories more of energy than does the 18.016 grms. of ice which they form if united, and which occupies a volume of 19.21 cc.

There is no supposition whatever connected with this fact, except the slight uncertainty due to the measurements and their extrapolation, and this uncertainty is probably not greater than 100 calories. A study of substances

\* A Paper read at the Fourteenth General Meeting of the American Electrochemical Society.



with higher melting-points confirms the view that the errors introduced by the extrapolation are very slight, and we feel confident in the practical accuracy of our statement.

The total energy possessed by the hydrogen and oxygen at  $-273^{\circ}\text{C.}$  is probably very much more than 67,300 calories, and may be many times that amount, for we have no evidence whatever as to the energy which the ice possesses at that temperature. We only know that the energy of the ice is 67,300 calories less than the amount possessed by the equivalent hydrogen and oxygen before the combination. The ice may, and in our opinion certainly does, possess a vast amount of energy. Its store of energy is perhaps comparable to that possessed by radium.

In what form does the 67,300 calories of energy possessed by the 34.78 cc. of hydrogen and oxygen at  $-273^{\circ}\text{C.}$  exist? The answer to the question, "What is energy?" and "What is matter?" must both be given before any sufficient answer to the first question could be made. But there is certainly no harm in stating what we do know concerning the answer to that question, and it is this:—

If the same mechanical laws which govern larger masses of matter and energy at higher temperatures apply to the hydrogen and oxygen at  $-273^{\circ}\text{C.}$ , then a stable system could not exist if all of the energy were kinetic, or if all of the energy were potential, but some portion of the energy must be potential and some portion must be kinetic (see Meyer, "Kinetic Theory of Gases," p. 344, English translation of second revised edition).

There has never been the slightest evidence produced to show that these mechanical laws do cease to hold at  $-273^{\circ}\text{C.}$ , or with small sub-divisions of mass, and therefore we think it probable that at  $-273^{\circ}\text{C.}$  the small particles—atoms if you please to call them so—of hydrogen and oxygen, are in exceedingly rapid motion, and are held together by some force which gives rise to a potential energy. The force we will call chemical affinity, and the energy we will call chemical energy.

It is not out of place to point out here, for it is very suggestive, that if we have two masses of matter which attract each other inversely as the square of their distance apart, and which form a stable system, they will revolve around their common centre of gravity, and *they cannot give out a greater amount of energy than they retain as kinetic energy.* Just what relation would hold if we had numerous particles governed by the same laws, mathematics has not yet proved adequate to reveal. The relation may be a very simple one in spite of the mathematical complexity of the problem.

The answer to our first question is therefore that 67,300 calories of the total energy possessed by the 2.016 grms. of hydrogen and the 16 grms. of oxygen at  $0^{\circ}\text{C.}$  existed in some form in those substances at  $-273^{\circ}\text{C.}$ , and 4097 calories of energy were added in raising those substances to  $0^{\circ}\text{C.}$  and changing them to the gaseous condition.

#### Energy Changes caused by a Rise in Temperature.

We wish next to show why 4097 calories of energy were necessary to change the temperature and condition of the hydrogen and oxygen as described.

Of this amount of energy 2125 calories were added to the hydrogen. Now the hydrogen at  $-273^{\circ}\text{C.}$  originally occupied a volume of 24.18 cc., and at  $0^{\circ}\text{C.}$  it occupied a volume of 22.431 cc. This expansion necessitated the expenditure of work in pushing back the atmosphere. The work so done we will call  $E_t$ , and it may be calculated for 1 gm. from the equation (see Note)—

$$E_t = 0.000031833 P (V - v) \text{ calories} \quad (1),$$

where  $P$  is the pressure in mm. of mercury, and  $V$  is the final and  $v$  the original volume. For hydrogen, therefore, the external work performed during the expansion is  $0.000031833 \times 760 (11.1264 - 12.1) 2.016 = 542.1$  calories.

(NOTE.—The constants used in this paper are:—Density of mercury = 13.5956 at  $0^{\circ}$  referred to water at  $4^{\circ}\text{C.}$ ; attraction of gravity = 980.5966 at latitude  $45^{\circ}$  and sea-level; atomic weight of oxygen = 16.00; density of hydrogen at latitude  $45^{\circ}$  and sea-level = 0.0000898765. This is an average of the values given by Morley, ("Smithsonian Contributions to Knowledge," No. 980), and the value given by Rayleigh (*Proc. Roy. Soc.*, liii., 147, No. 322), after reduction to latitude  $45^{\circ}$ . Rayleigh's value was an average of his own value, that of Leduc, and the value of Regnault as corrected by Crafts. The unit calorie is taken as from  $15^{\circ}$  to  $16^{\circ}\text{C.}$ , and as equal to 41,880,000 ergs. This is Rowland's value as corrected by Day—*Phys. Rev.*, 1898, vi., 194; see also *Ber. Deut. Phys. Ges.*, vi., 578).

During the expansion of the hydrogen the molecules of the hydrogen were moved further apart, and a certain amount of energy was necessary to overcome the attraction between the hydrogen molecules. This amount of energy, which we will denote by  $E_a$ , may be calculated, as the author has shown in a series of papers,\* from the equation—

$$E_a = \mu' (\sqrt[3]{d} - \sqrt[3]{D}) \text{ calories} \quad (2)$$

where  $d$  and  $D$  are the density in the original and final conditions respectively, and  $\mu'$  is a constant which may be obtained from the following equation:—

$$\frac{L - E_t}{\sqrt[3]{d} - \sqrt[3]{D}} = \mu' \quad (3).$$

Here  $L$  is the heat of vaporisation,  $E_t$  is the energy spent in pushing back the atmosphere during the vaporisation, and is calculated from Equation 1,  $d$  is the density of the liquid, and  $D$  the density of the saturated vapour at the temperature of vaporisation.

To calculate  $\mu'$  for hydrogen,  $L = 123.1$  calories. The density of the liquid at its boiling-point has been determined by Dewar as 0.070025, corresponding to a volume of 14.28 cc. per gm. The density of the saturated vapour may be calculated on the supposition that it obeys the gas laws, the error so introduced being negligible. The equation for this calculation is:—

$$D = \frac{0.000016014 P_m}{T} \quad (4).$$

Since  $T$  is  $20.41^{\circ}$ ,  $D$  becomes 0.001202, and the corresponding volume is 831.9 cc. From Equation 1,  $E_t$  is found to be 19.78 calories, and  $L - E_t$  is therefore 103.32. Dividing this by the value of  $\sqrt[3]{d} - \sqrt[3]{D}$ , namely, 0.3059, we have for  $\mu'$  the value 337.7. Substituting this value in Equation 2, and using for  $d$  the density of hydrogen at  $-273^{\circ}\text{C.}$  as given by Dewar, 0.0000898765, and for  $D$  the value already given at  $0^{\circ}$  under standard conditions, namely, 0.00008988, we have finally,—

$$E_a = 337.7 \times 0.3909 \times 2.016 = 266.1 \text{ calories.}$$

It is not necessary to pause here to defend the kinetic theory of gases. That theory represents the attempt to extend the mechanical laws which govern large masses of matter to smaller particles of the same material. Its foundation upon these mechanical laws is quite as secure as are the foundations of any system of thermodynamics yet advanced—both theories alike resting upon observed laws to which no single exception has ever been found. Moreover, it has led to important discoveries and correlated numerous facts.

Making use now of the kinetic theory, it is easy to calculate the energy necessary to add to the gm. molecular

\* *Journ. Phys. Chem.*, 1902, vi., 209; 1904, viii., pp. 383, 593; 1905, ix., 402; 1906, x., 1; 1907, xi., pp. 132, 594. The equation has been proved to hold for liquids as they expand to the volume of the saturated vapour. The author believes that the equation, which was theoretically derived, may be applied as above, and the result appears to justify the belief.



weight of hydrogen in order that its molecules should have at  $0^{\circ}\text{C}$ . sufficient motion to produce the pressure which we know is produced at that temperature. Using the constants which we have adopted, and calling this kinetic energy  $E_k$ , the equation takes the form—

$$E_k = \frac{3RT}{2} = \frac{2 \cdot 9817 T}{m} \text{ calories.} \quad (5).$$

Whence the kinetic energy of the grm. molecular weight of hydrogen at  $0^{\circ}\text{C}$ . is  $814 \cdot 0$  calories.

We know also from the kinetic theory of gases that whenever we increase the kinetic energy of a molecule we at the same time increase its internal energy, which we will call  $E_i$ . The increase in the internal energy is proportional to the increase of the kinetic theory, and its amount may be calculated from the relation first proposed by Waterston, namely, —

$$\gamma = \frac{\text{specific heat of gas at constant pressure}}{\text{specific heat of gas at constant volume}} = \quad (6).$$

$$\frac{S_p}{S_v} = \frac{3/2 R + E_i + R}{3/2 R + E_i} = \frac{5/2 R + E_i}{3/2 R + E_i}.$$

Now putting in the place of  $R$  its value  $2/3 \frac{E_k}{T}$ , and solving for  $E_i$ , we obtain finally, since  $T$  is equal to 1:—

$$E_i = \frac{5/3 - \gamma}{\gamma - 1} E_k \text{ calories} \quad (7).$$

For hydrogen  $\gamma = 1 \cdot 4084$  from the measurements of Lummer and Pringsheim ("Smithsonian Contributions to Knowledge," No. 1126), and so we have for  $E_i$  for  $2 \cdot 016$  grms. of hydrogen,  $514 \cdot 6$  calories.

As a summary, therefore, we have for the total energy necessary to change  $2 \cdot 016$  grms. of hydrogen from the solid condition at  $-273^{\circ}\text{C}$ . to the gaseous condition at  $0^{\circ}\text{C}$ . under  $760$  mm. pressure:—

|                                                                   | Calories.        |
|-------------------------------------------------------------------|------------------|
| $E_e$ = energy necessary to overcome external pressure .. .. .    | $= 542 \cdot 1$  |
| $E_a$ = energy necessary to overcome molecular attraction .. .. . | $= 266 \cdot 1$  |
| $E_k$ = Energy necessary for translational motion .. .. .         | $= 814 \cdot 0$  |
| $E_i$ = Energy necessary for internal work ..                     | $= 514 \cdot 6$  |
| Total .. .. .                                                     | $= 2136 \cdot 8$ |

Now, as a matter of observation, we found that  $2125$  calories were added to effect the above mentioned change in the condition of the hydrogen, and the agreement is certainly within the limit of experimental errors involved in the measurements.

An exactly similar calculation regarding the energy added to the oxygen can be made from the following data:—

|                                                                  |                        |
|------------------------------------------------------------------|------------------------|
| Density of solid at $-273^{\circ}\text{C}$ . .. .                | $= 1 \cdot 5154$ (a)   |
| Density of liquid at boiling-point .. .                          | $= 1 \cdot 134$ (b)    |
| Density of vapour at its boiling-point .. .                      | $= 0 \cdot 00440$ (c)  |
| Density of oxygen at $0^{\circ}\text{C}$ . .. .                  | $= 0 \cdot 001429$ (d) |
| Boiling-point of oxygen ( $^{\circ}\text{C}$ .) .. .             | $= -182 \cdot 8$ (e)   |
| $\gamma$ = ratio of specific heats of this gas .. .              | $= 1 \cdot 4025$ (f)   |
| Heat of vaporisation of oxygen at boiling-point (calories) .. .  | $= 50 \cdot 97$ (g)    |
| From the above $L - E_e = 45 \cdot 49$ calories, and $\mu'$ .. . | $= 51 \cdot 74$        |

(a) Dewar, *Proc. Roy. Soc.*, 1904, lxxiii., 251.

(b) Ladenburg and Krügel, *Ber.*, 1899, xxxii., 1415.

(c) Dewar, *Proc. Roy. Soc.*, 1904, lxxiii., 255.

(d) For authorities, see footnote on the density of hydrogen, p. 19.

(e) See Note (a), Table I.

(f) Müller, "Dissertation," Breslau, 1882.

(g) See Note (e), Table I.

We have, finally, for the energy necessary to change  $1$  grm. of oxygen from the solid condition at  $-273^{\circ}\text{C}$ . to the gaseous condition at  $0^{\circ}\text{C}$ . and under  $760$  mm. pressure:—

|                                                                   | Calories.        |
|-------------------------------------------------------------------|------------------|
| $E_e$ = Energy necessary to overcome external pressure .. .. .    | $= 16 \cdot 89$  |
| $E_a$ = Energy necessary to overcome molecular attraction .. .. . | $= 53 \cdot 62$  |
| $E_k$ = Energy necessary for translational motion .. .. .         | $= 25 \cdot 44$  |
| $E_i$ = Energy necessary for internal work ..                     | $= 16 \cdot 69$  |
| Total .. .. .                                                     | $= 112 \cdot 64$ |

To effect the above mentioned change for  $16$  grms. of oxygen will require  $1802$  calories. The amount actually added to the oxygen was found to be  $1972$  calories.

The divergence here, amounting to about  $10$  calories per grm., cannot, we believe, be considered as entirely due to experimental error, and we have made an extended investigation as to its cause. As a result of this investigation, the details of which it would be impossible to reproduce within the limits of this paper, we believe that besides the so-called external, attractive, kinetic, and internal energy, for which allowance has been made, *all* bodies, while in the solid condition, require yet an additional amount of energy, the exact office of which we are unable to explain. The amount of this unaccounted for energy varies with the absolute temperature of the melting-point of the body. In the case of hydrogen because of its very low melting-point,  $14^{\circ}$  absolute, the amount thus unaccounted for was well within the limit of experimental error. But with oxygen this is not the case.

We are led here to add that the total energy necessary to change a solid monatomic element from  $-273^{\circ}$  to the liquid condition at its melting-point, appears to us to be three times the kinetic energy of translation required by the element at that temperature; or, in other words,  $8 \cdot 94 T$  calories, where  $T$  is the absolute temperature of the melting-point. Prof. J. W. Richards (*Trans. American Electrochem. Soc.*, 1908, xiii., 447) has reached nearly the same conclusion, considering the total heat in the molten metal at its melting-point to be  $10 T$  calories. We will publish our data and conclusions upon this subject later.

Unfortunately our calculations cannot be extended to water, for it is an associated substance.

Except for the discrepancy of  $170$  calories, we have shown why and how the  $4097$  calories of energy added to the hydrogen and oxygen to change them from their condition at  $-273^{\circ}\text{C}$ . to their condition at  $0^{\circ}\text{C}$ . were expended, and have therefore, in part at least, answered the second question as to why and how the amount of heat given out by the reaction of the hydrogen and oxygen will vary under different conditions of volume, temperature, and pressure.

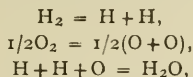
#### The Chemical Changes Involved in the Reaction.

The answer to the third question, as to why the reaction did not take place when the hydrogen and oxygen were first mixed, and before the passage of the electric spark, has doubtless occurred to everyone. It was first necessary to loosen the union of some of the hydrogen atoms from their combination with other hydrogen atoms, and the union of some of the oxygen atoms from their combination with other oxygen atoms. Then, once free, the hydrogen atoms and the oxygen atoms unite, and in so doing give out enough heat to loosen the neighbouring hydrogen and oxygen molecules, and these in their turn unite, and thus the reaction is propagated.

But it is perhaps not so clearly recognised, that the force which we call chemical affinity is probably never directly affected by a rise in temperature. Certainly in the case under consideration we have accounted for all of the energy added to the hydrogen and the oxygen from  $-273^{\circ}$  to  $0^{\circ}\text{C}$ ., save  $170$  calories, as having been used to effect

external work, overcome molecular attraction, and effect an increase in the translational and internal motion of the molecules, and the original 67,300 calories possessed at 273° C. appears to have been held, intact as it were, neither increased nor diminished, by the changes of temperature, pressure, and volume necessary to raise the hydrogen and oxygen to their condition at 0° C.

The 67,300 calories represents the total energy change of the three chemical reactions—



when taking place at - 273° C.

We cannot at present determine how much energy would be required by each reaction if it alone took place, but when a sufficient number of well-chosen chemical reactions have been thus studied it may be possible to find the key to all, and to determine not alone the force which acts between any two atoms, but the law which governs the distance apart of the atoms as well, and the exact amount of energy which will be given out by the different chemical and physical changes involved. A study of the energy changes accompanying, and the conditions necessary for, the dissociation of simple molecules should greatly aid in the solution of the problem.

(To be continued).

## PROCEEDINGS OF SOCIETIES.

### CHEMICAL SOCIETY.

Ordinary Meeting, December 21st, 1911.

Prof. PERCY F. FRANKLAND, LL.D., F.R.S., President, in the Chair.

MESSRS. Hugh Marshall and C. H. K. Gonville were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Fred Barrow, M.Sc., Ph.D., Birkbeck College, Breems Buildings, E.C.; David Brownlie, B.Sc., 41, Corporation Street, Manchester; Thomas Alfred Brunjes,

Road, Garston, Liverpool; Jyotish Chandra Ghosh, 105, M. C. Ghosh's Lane, Howrah, India; Richard Ernest Gibbins, Clytha, Quinton Road Coventry; Rupert William Pope, B.Sc., 10 Malpas Road, Brockley, S.E.; Howard Vincent Potter, Rosemount, Pollard Road, Whetstone, N.; Alfred Reginald Roberts, care of Canada Cement Co., Shallow Lake, Ontario; Richard Smith, 6, Essex Road, Gorton, Manchester; John Kerfoot Wood, D.Sc., 7, Airlie Terrace, Dundee.

A certificate has been authorised by the Council for presentation to ballot under By-law I. (3) in favour of John Duncan, Victoria Street, Waterloo, Sydney, N.S.W.

The PRESIDENT announced that the Longstaff Medal (1912) had been awarded to Dr. H. Brereton Baker, F.R.S.; the actual presentation would be made at the Annual General Meeting of the Society in March, 1912.

Of the following papers those marked \* were read:—

\*333. "Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part II. The Rotations of some Secondary Alcohols containing the Isopropyl Group." By ROBERT HOWSON PICKARD and JOSEPH KENYON.

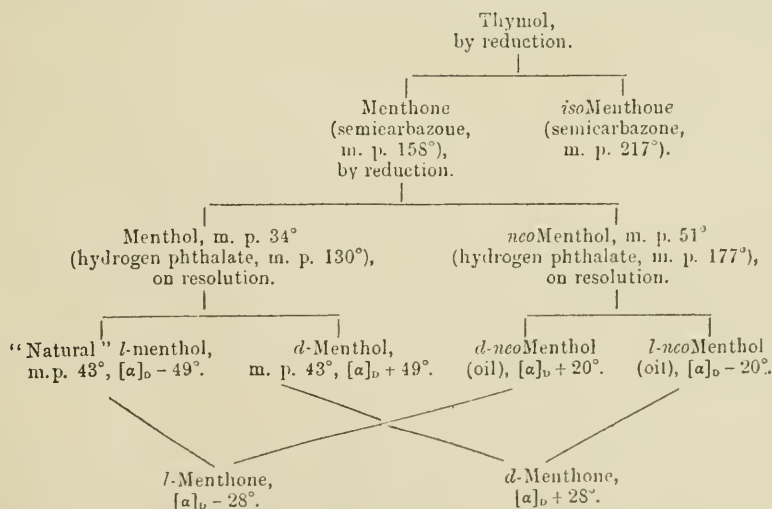
The authors have continued their investigations (*Trans.*, 1911, xcix., 45), and six alcohols of the general formula  $\text{CHMe}_2\text{CH}(\text{OH})\cdot\text{R}$ , where R = methyl, ethyl, *n*-propyl, *n*-amyl, *n*-hexyl, or *n*-octyl, were described.

The specific rotations at 20° of the dextrorotatory forms these alcohols are:—Methylisopropylcarbinol,  $[\alpha]_D + 4.8^\circ$ ; ethylisopropylcarbinol,  $[\alpha]_D + 15.1^\circ$ ; propylisopropylcarbinol,  $[\alpha]_D + 21.2^\circ$ ; *n*-amylisopropylcarbinol,  $[\alpha]_D + 22.7^\circ$ ; *n*-hexylisopropylcarbinol,  $[\alpha]_D + 21.5^\circ$ ; and *n*-octylisopropylcarbinol,  $[\alpha]_D + 18.5^\circ$ .

\*334. "The Alcohols of the Hydroaromatic and Terpene Series. Part II. The Menthols corresponding with Optically Inactive Menthone." By ROBERT HOWSON PICKARD and WILLIAM OSWALD LITTLEBURY.

The authors described an investigation of the relationship existing between the menthols produced by the reduction of one of the two optically inactive stereoisomerides, which have the formula  $\text{CHMe} < \begin{smallmatrix} \text{CH}_2 - \text{CO} \\ \text{CH}_2 \cdot \text{CH}_2 \end{smallmatrix} > \text{CHPh}^\beta$ . The accompanying diagram shows the results obtained.

*d*-*neo*Menthol was found in some residues which were kindly presented to the authors by Messrs. Schimmel and Co., who obtained the same after working up large quantities of Japanese peppermint oil for *l*-menthol.



49, St. Donatts Road, New Cross, S.E.; Sidney Waterfield Bunker, B.Sc., 30, York Street, Twickenham; Tom Peach Colclough, M.Sc., 47, Vicar Lane, Woodhouse, Sheffield; Cornelius Durham Garbutt, 2, Hartington

\*335. "The Absorption Spectra of Quinine, Cupreine, 6-Methoxyquinoline, and 6-Hydroxyquinoline." By JAMES JOHNSTON DOBBIE and JOHN JACOB FOX.

In a paper dealing with the absorption spectra of



cinchonine, quinine, and their isomerides (*Trans.*, 1911, xcix., 1254), it was shown that the absorption spectra of cinchonine and quinoline are practically identical, the reduced half of the cinchonine molecule having little effect on the spectrum. The absorption spectra of quinine and cupreine have now been compared with those of 6-methoxyquinoline and 6-hydroxyquinoline, with similar results.

The four spectra resemble one another very closely. They exhibit three bands each, the principal band having its head at about  $1/\lambda 3050$ , and the two others at about  $1/\lambda 3500$  and  $1/\lambda 3750$  respectively. The chief difference between the spectra of quinine and cupreine on the one hand, and those of methoxyquinoline and hydroxyquinoline on the other, lies in the somewhat greater absorption exhibited by the alkaloids. The hydrochlorides of quinine and 6-methoxyquinoline also yield absorption spectra which are nearly identical. Those given by N/100 solutions of quinine sulphate and methoxyquinoline sulphate (both fluorescent solutions) differ only in the greater general absorption of the former.

\*336. "Amino-derivatives of Arylsulphonanilides and Arylsulphon- $\beta$ -naphthalides." By GILBERT T. MORGAN and FRANCES M. G. MICKLETHWAIT.

The toluene- $p$ -sulphonyl derivatives of the *m*- and *p*-nitroanilines are readily methylated with methyl halides in alcoholic soda or potash, and the corresponding *as*-toluene- $p$ -sulphonylmethyl-*m*(and *p*)-phenylenediamines are produced by the reduction of these toluene- $p$ -sulphonylmethylnitroanilines. The diazonium salts of the new bases furnish azo-colours dyeing on wool or silk by coupling with various naphtholsulphonic acids.

Toluene- $p$ -sulphon- $\beta$ -naphthalide yields on nitration not only toluene- $p$ -sulphonyl-1-nitro- $\beta$ -naphthylamine, but also toluene- $p$ -sulphonyl-1:6-dinitro- $\beta$ -naphthylamine. The former of these nitro-derivatives is readily methylated, the latter only with some difficulty.

The amines produced by reducing these nitro-compounds and their alkyl derivatives were described, together with a similar series of compounds derived from  $\beta$ -naphthylamine-6-sulphonic acid.

337. "The Action of Nascent Hydrogen on Nitric Acid." By MARINDRA NATH BANERJEE and SATISH CHANDRA BANERJEE.

Veley, in explaining the action of nitric acid on metals (*Proc. Roy. Soc.*, 1890, xlvii., 216; 1893, lii., 27; *Phil. Trans.*, 1891, A, 312; *Journ. Soc. Chem. Ind.*, 1891, x., 204), states that the action is due to nitrous acid and to its mass present in the solution. He believes that the action is started with mere traces of nitrous acid, always present in the original acid. He is not in favour of the nascent hydrogen theory advanced by certain chemists. The authors find that nascent hydrogen has rapid action on nitric acid, first decomposing it (acting catalytically), and then reducing it to the lower oxides of nitrogen, and finally to ammonia. This argument has been further extended to explain the action of nitric acid on metals, in which the authors have attempted to prove that it is the nascent hydrogen, and not nitrous acid, that is responsible for the formation of various reduction products. The reaction is found to depend entirely on the capacity of metals to decompose water, and the authors confirm the views of Montemartini as to the relation of the action of nitric acid on metals to that of metals on water (liberating hydrogen), namely, that those metals which decompose water at a high temperature give with nitric acid, nitrogen peroxide, trioxide, and dioxide; whilst those that decompose water at a low temperature give, in addition to the above, nitrous oxide, nitrogen, and ammonia; and, lastly, those decomposing water at the ordinary temperature also evolve hydrogen.

Nascent hydrogen was obtained from platinum-black which had occluded the gas. The experiments showing the interaction between nitric acid and the platinum-black on the one hand, and the absorption of the products by suitable reagents on the other, were conducted in a

suitably arranged apparatus. The interaction of the nascent hydrogen and nitric acid results in the ready decomposition of the acid and formation of various reduction products, the free oxygen being wholly converted into water.

338. "Studies in the Camphane Series. Part XXXI. Condensation of Camphorquinone with Nitromethane, Ethyl Cyanoacetate, and Phenylacetoneitrile." By MARTIN ONSLOW FORSTER and JOHN CHARLES WITHERS.

Nitromethylenecamphor,  $C_8H_{14}$   $\begin{array}{c} \diagup C:CH \cdot NO_2 \\ \diagdown CO \end{array}$ , prepared

from camphorquinone and sodionitromethane in alcohol, melts at  $77^\circ$ , and is immediately resolved into its factors by warm aqueous alkali; under certain conditions it is accompanied by nitromethylhydroxycamphor,

$C_8H_{14}$   $\begin{array}{c} \diagup C(OH) \cdot CH_2 \cdot NO_2 \\ \diagdown CO \end{array}$ , which melts at  $104^\circ$ , and also

gives camphorquinone with hot alkali hydroxide. Ethyl camphorylidenecyanoacetate (ethyl methylenecamphorcyano-

carboxylate),  $C_8H_{14}$   $\begin{array}{c} \diagup C:C(CN) \cdot CO_2 \cdot C_2H_5 \\ \diagdown CO \end{array}$ , produced by

the influence of sodium ethoxide (0.05 mol.) on an alcoholic mixture of camphorquinone and ethyl cyanoacetate, forms lustrous sulphur-yellow prisms, melting at  $97^\circ$ . The corresponding acid,  $C_{13}H_{15}O_3N$ , melts at  $141-143^\circ$ , and the methyl ester,  $C_{14}H_{17}O_3N$ , at  $81^\circ$ . Phenylcyano-

methylenecamphor,  $C_8H_{14}$   $\begin{array}{c} \diagup C:C(CN) \cdot C_6H_5 \\ \diagdown CO \end{array}$ , obtained from

camphorquinone and phenylacetoneitrile with a small proportion of sodium ethoxide, crystallises in massive yellow prisms, melting at  $166^\circ$ .

When ethyl camphorylidenecyanoacetate is treated with hydrogen peroxide, hydrolysis of the cyano-group takes place simultaneously with oxidation. The resulting amide-ester,  $C_{15}H_{21}O_6N$ , melts at  $209^\circ$ , and is accompanied by the amide-acid,  $C_{13}H_{17}O_6N \cdot H_2O$ , melting at  $205^\circ$ . Both substances, on complete hydrolysis, yield the dibasic acid,  $C_{13}H_{16}O_7$ , which melts at  $231^\circ$ .

339. "Solutions of Halogen Double Salts in Water and Ether." By JAMES ERNEST MARSH.

The capability of the halogen double salts to give homogeneous solutions in a mixture of ether and water is limited, on the one hand, by the too great solubility of the salt in one of the solvents, and on the other by the too slight solubility of the salt in both solvents. Sodium, potassium, rubidium, and barium mercuri-iodides give with ether and water homogeneous solutions, which on warming separate into three layers; the lithium and ammonium salts are very soluble in ether with a little water, and leave the excess of water undissolved; the caesium salt is only sparingly soluble, and has but little effect on a mixture of ether and water. Of the bromides, ammonium mercuri-bromide, and of the chlorides, lithium mercurichloride are the only inorganic salts of this sort which have been found to give homogeneous solutions, separating on warming into three layers. Potassium mercurichloride resembles caesium mercuri-iodide, and has but little action. So far as they have been examined, the salts of primary amines resemble the salts of ammonium, whilst tetramethylammonium mercuri-iodide resembles the caesium salt, and has even less action.

340. "The Relation between the Absorption Spectra of Metallic Ions and their Valency." By CECIL REGINALD CRYMBLE.

The absorption spectra of the aqueous solution of more than thirty metals have been examined. It has been found that the metals of constant valency give solutions which are non-absorptive provided that a salt is employed, the acidic radicle of which is itself diactinic. On the other hand, the metals which vary in valency yield absorptive solutions. A connection has also been shown to exist



between the absorptive properties of solution of metals and the chemical and physical properties of the metals.

341. "The Solubility of Electrolytes in Aqueous Solutions. Part II. Solubility of Oxalic Acid in other Acids." By JAMES IRVINE ORME MASSON.

In extension of previous work, which dealt with salts in acid solution (*Trans.*, 1911, xcix., 1132), measurements have been made of the solubility at 30° of oxalic acid in solutions of nitric and of hydrochloric acids.

In both cases the solubility falls to a minimum as the concentration of solvent acid rises, after which it increases. In nitric acid solutions this increase is terminated by conversion of the solid oxalic acid into the anhydrous compound, the solubility of which then falls to a second minimum. The concentration of nitric acid at the transition point is about that of "constant boiling-point" acid.

The solubility curves of the dihydrate in both acids are conic in form, and in this respect resemble certain other solubility curves.

The assumption of constant molecular volume in solution, which was found to be valid in the earlier cases studied, holds also in these instances.

Supplementary determinations were made with  $\beta$ -naphthalene-sulphonic acid in hydrochloric acid solution. The curve obtained resembles those for the salt-acid examples.

342. "The Determination of Sulphur in Petroleum." By JAMES MCCONNELL SANDERS.

The Mahler or Hempel calorimetric bomb method for estimating the total sulphur in petroleum, although trustworthy, is somewhat lengthy, since the gaseous combustion products must be absorbed, and when samples poor in sulphur are under treatment, several combustions must be made. The Parr calorimeter is not available for petroleum on account of the small amount of sample which can be treated.

The author described a method by which a large sample may be concentrated by treatment with fuming nitric acid and potassium bromide, the product being absorbed by magnesium oxide, which enables it to be readily removed from the concentrating dish, and burnt in the Parr apparatus with sodium peroxide. Several samples may be treated simultaneously, the final combustion taking about forty-five seconds.

Test analyses were given, comparing results with the Mahler bomb method. For samples poor in sulphur a modified lamp method was described, in which a large sample is completely burnt, thus avoiding the errors in the usual method owing to the sulphur being given off in an irregular manner.

Some Mexican and Texan kerosenes contain loosely combined sulphur, which decomposes when heated or when in contact with some metals, such as copper; since samples have been known to blister, and even perforate, a copper lamp, the testing of commercial kerosenes for such unstable sulphur was recommended. The author described a qualitative and quantitative method for the purpose.

For the manipulation of the small precipitates of barium sulphate obtained in these operations, the author described a rapid suction-filter method, in which the amount of filter-paper is reduced to a minimum, and the weighing conducted in a very light dish. For the simultaneous treatment of several precipitates a special arrangement of the apparatus was described.

#### RÖNTGEN SOCIETY.

At the meeting of the Röntgen Society on January 2nd, Mr. SIDNEY RUSS, B.Sc., of the Cancer Research Laboratory, Middlesex Hospital, gave what was apparently something in the nature of an interim report upon X-ray and Radium Measurements and Comparisons. Part of the object of the investigations was to determine whether, with an X-ray bulb, it would be possible to obtain any sort of equivalent in terms of  $\beta$ - and  $\gamma$ -rays from a definite

point. The first portion of the paper related to the relative absorption of X-rays and the  $\beta$ - and  $\gamma$ -rays of radium by different thicknesses of aluminium. The second portion was a comparison of the ionisation produced by X-rays from an ordinary focus-tube, and that caused by the  $\gamma$ -rays from a measured quantity of radium, and the third portion was a comparison of what may be termed equivalent biological doses of X-rays,  $\beta$ -rays, and  $\gamma$ -rays. An interesting point was brought out in connection with the measurements of relative penetrability, namely, that the penetration of the rays from an X-ray bulb was much more of the order of penetration of the  $\beta$ -rays than of that of the  $\gamma$ . Mr. Russ had no doubt that other experimenters had worked with a higher spark-gap—his own had ranged from one of 4½ cm. to one of 19 cm.—but so far as they had gone his experiments suggested that the X-rays fell rather on the  $\beta$ -ray side of radium than on the  $\gamma$ -ray side. Comparing equivalent biological doses, Mr. Russ divided them into two categories, namely, those in which the condition dealt with was at the surface, necessitating the employment of unscreened radiation, and those relating to deep-seated conditions. After allowing for the distance factor in the case of the X-rays—a factor which quickly reduced their apparent advantage over the rays of radium—Mr. Russ came to the following conclusion:—In equivalent times the same biological effect per square cm. of tissue on the surface ought to be obtained by an exposure to  $\beta$ -rays of radium corresponding to 2.75 mgrms. of radium bromide as by the exposure of X-rays from an unscreened bulb working at 9 cm. spark-gap, with a distance of 10 cm. between the anode and the tissue.

#### NOTICES OF BOOKS.

*Allen's Commercial Organic Analysis.* Volume V., Fourth Edition. Edited by W. A. DAVIS, B.Sc., A.C.G.I., and SAMUEL S. SADTLER, S.B. London: J. and A. Churchill. 1911. (21s. net).

ALTHOUGH the fifth volume of "Allen's Commercial Organic Analysis" was revised comparatively recently it has been completely re-written for the fourth edition, and while retaining the original form contains a large amount of additional matter. It includes sections on tannins, leather, dyes and colouring matters, and inks, and the official methods of analysis used in Europe and in the United States are accurately described. A new and complete section has been devoted to the detection of colouring matters in foods.

*An Experimental Course of Physical Chemistry.* Part I. By JAMES FREDERICK SPENCER, D.Sc. (Liverpool), Ph.D. (Breslau). London: G. Bell and Sons, Ltd. 1911. (3s. 6d).

THIS book will certainly find a hearty welcome in chemical laboratories, for many demonstrators have felt the need of just such a guide to put into the hands of their students. It is most essential that the student should get some acquaintance with, and practice in, the simpler experiments in physical chemistry, and that his inorganic practical work should not be entirely limited to analysis and preparations. Practical physical chemistry has the advantage of providing excellent opportunity for acquiring accuracy and neatness of manipulation, besides fixing upon the student's mind important general principles. In this part of the book only statical experiments are described, and of them a good variety is given, so that the demonstrator can choose which a particular student or class may perform, since it is by no means necessary nor even advisable for every student to work straight through the whole book. The experimental directions are sufficiently detailed and clear for all purposes, and the book is of a thoroughly practical type, and covers an extended course of physical chemistry.

**Pyrometry.** By CHARLES R. DARLING. London: E. and F. N. Spon, Ltd. New York: Spon and Chamberlain. 1911. (5s. net).

THE author of this book has had extensive experience of the use of pyrometers of various kinds, and is in a position to write a thoroughly practical handbook on the subject. The actual manipulation of the instruments is very fully described, only those which are found reliable in practice being chosen for lengthy treatment. Some account is given of the theory of the construction and use of pyrometers, and a chapter is devoted to each of the different types of instrument. The author impartially summarises the advantages and disadvantages of the different instruments, and gives some hints on the management of them. Many kinds of miscellaneous appliances are selected for brief description, and the book is one which is likely to be exceedingly useful to the increasing number of engineers and others who are interested in the measurement of high temperatures.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Atti della Reale Accademie dei Lincei.*  
Vol. xx., No. 8, 1911.

**Addition Products of Derivatives of Trinitrobenzene with Aromatic Nitrogen Compounds.**—R. Ciusa and L. Vecchiotti.—The study of the addition products of the hydrazones with aromatic polynitro derivatives shows that picryl chloride always adds itself on by two molecules, unless there is a nitro-group in the aldehyde residue. The introduction of a nitro-group in the phenyl hydrazine residue instead does not have the same effect. Thus the *p*-nitrophenyl hydrazone of benzaldehyde combines with two molecules, while the phenylhydrazone of *m*-nitrobenzaldehyde combines with only one molecule of picryl chloride. The methylphenyl hydrazone of benzoic aldehyde unites with two molecules of picric chloride, and that of piperonal with one molecule. With regard to other trinitrobenzene derivatives, two molecules are added on to benzalphenyl hydrazone, cinnamylidene phenyl hydrazone and *p*-tolylbenzal hydrazone. All other hydrazones unite with only one molecule of nitro-derivative. Methylphenyl hydrazones give unstable addition products.

**Contribution to the Study of the Formation of Alkaloids in Tobacco.**—C. Ravenna and V. Babini.—The authors have determined the amount of nicotine in tobacco plants, which were treated as follows:—i. Roots immersed in a solution containing calcium nitrate, 1 gm.; potassium chloride, magnesium sulphate, mono-potassium phosphate, each 0.25 gm.; ferric chloride, a trace, and exposed to light. ii. Without the nitrate solution and exposed to light. iii. With the nitrate solution in darkness. iv. With the nitrate solution and 2 per cent glucose in the light. v. With the nitrate solution and 2 per cent glucose in the dark. The results obtained did not warrant the drawing of any definite conclusions, but it seems probable that the quantity of nicotine reaches a maximum for the plants supplied with glucose and exposed to light, and a minimum for those with glucose in the dark.

**Density and Refraction of System Furfural + Water.**—F. Schwes.—Dilute solutions of furfural show a slight decrease of density at all the temperatures investigated. The general shape of the temperature-density curve indicates a diminution in the decrease as the temperature increases. After 55° each curve shows a tendency to become parallel to the *x*-axis. At a given temperature, and for a given wave-length, the constant of refraction is practically constant. Its mean value at a given temperature varies according to the wave-length, and the difference in its value for different wave-lengths is independent of the concentration.

**Absorption Spectra of Complex Inorganic Salts.**—Elena Valla.—The author has studied the absorption spectra of some cobalt ammonium salts, and has found that the coefficient of absorption varies with the concentration. With every salt used there was a maximum at from 18 to 21 of the scale. The scale was graduated as follows:—

|                             | Scale line. | Wave-length. |
|-----------------------------|-------------|--------------|
| $\alpha$ -Strontium line .. | 9.50        | 6060         |
| Yellow sodium line ..       | 11.20       | 5896         |
| Green thallium line ..      | 16.00       | 5350         |
| $\delta$ -Strontium line .. | 27.90       | 4607         |

## MISCELLANEOUS.

**Royal Institution.**—On Tuesday next, January 16, at 3 o'clock. Prof. William Bateson will begin a course of six lectures at the Royal Institution on "The Study of Genetics"; on Thursday, January 18, Prof. A. W. Bickerton begins a course of two lectures on "The New Astronomy"; and on Saturday, January 20, the Rev. John Roscoe commences a course of two lectures on "The Banyoro, a Pastoral People of Uganda—(1) The Milk Customs; (2) Birth and Death Customs." The Friday Evening Discourse on January 19 will be delivered by Prof. Sir James Dewar on "Heat Problems," and on January 26 by Prof. Bertram Hopkinson on "The Pressure of a Blow."

**London Chamber of Commerce.**—A meeting of the Chemical Trade Section of this Chamber will take place at Oxford Court, Cannon Street, E.C., on Tuesday, January 16th, 1912, at 3 p.m., to consider the following Agenda:—Minutes; Correspondence; Election of Chairman; Election of Deputy Chairman; International Congress of Applied Chemistry (to consider, on a reference from the General Purposes Committee, an invitation to the Chamber as to the appointment of representatives to attend this Congress, and to take any necessary action); New Spirit Licences for Wholesale Druggists; Manufacture and Storage of Spirituous Preparations in Bond; other matters (if any).

## MEETINGS FOR THE WEEK.

- TUESDAY, 16th.**—Royal Institution, 3. "The Study of Genetics," by Prof. W. Bateson, F.R.S.
- WEDNESDAY, 17th.**—Royal Society of Arts, 8. "Illuminated MSS.," by Cyril Davenport, F.S.A.
- Microscopical, 8. President's Address, "On certain Blood Parasites."
- THURSDAY, 18th.**—Royal Institution, 3. "The New Astronomy," by Prof. A. W. Bickerton.
- Royal Society of Arts, 4.30. "The Old District Records of Bengal," by the Rev. Walter K. Firminger, B.D.
- Royal Society. "Physiological Effects of Low Atmospheric Pressures, as observed on Pike's Peak, Colorado," by J. S. Haldane, C. G. Douglas, Y. Henderson, and E. C. Schneider. "Effect of Altitude on the Dissociation Curve of the Blood," by J. Barcroft. "Note on *Astroclera wislizeni*, Lister," by R. Kirkpatrick. "*Herpetomonas pediculi*, nov. spec., Parasitic in the Alimentary Tract of *Pediculus vestimentis*, the Human Body Louse," by H. B. Fantham. "Antelope Infected with *Trypanosoma gambiense*," by Capt. A. D. Fraser and Dr. H. L. Duke.
- Chemical, 8.30. "Boiling-points of Mercury, Cadmium, Zinc, Potassium, and Sodium," by C. T. Heycock and F. E. E. Lamplough. "Formation and Reactions of Imino-compounds—Part XVII., The Alkylation of Imino-compounds," by J. F. Thorpe. "1:2-Diketohydrindene," by W. H. Perkin, W. M. Roberts, and R. Robinson. "Isonarcotine," by E. G. Jones, W. H. Perkin, and R. Robinson. "Esterification Constants of some Substituted Acetic and Benzoic Acids," by J. J. Sudborough and Miss M. K. Turner. "Aromatic Antimony Compounds—Part III., Primary Aryl Derivatives," by P. May.
- FRIDAY, 19th.**—Royal Institution, 9. "Heat Problems," by Sir James Dewar, F.R.S.
- SATURDAY, 20th.**—Royal Institution, 3. "The Banyoro, a Pastoral People of Uganda—(1) The Milk Customs," by The Rev. John Roscoe, M.A.



# THE CHEMICAL NEWS.

VOL. CV., No. 2721.

## NOTES ON PLANT CHEMISTRY.

By P. Q. KEEGAN, LL.D.

### *The Origin of the Lichen Acids.*

THE quite distinctive chemical specialty of lichens is the presence of what are called lichen acids, some of which afford the chromogen of well known domestic dyes. These acids are chiefly developed or excreted in the outermost cortical cells and on the upper surface of the reproductive organs (apothecia), *i.e.*, in such parts as are well exposed to the air. The acids are not contained in the cells themselves, but only appear on the cell walls and in certain small irregular corpuscles called granulations or gonimia, when these occur in the epithallus. It is important to notice that those lichens which produce relatively large quantities of oxalate of calcium have a proportionally small content of lichen acids. Some ninety-four of the latter belong to the aromatic series, while forty-nine belong to the fatty series. The special faculty of lichens to produce these very peculiar and elusive compounds is, according to Zopf, founded in all probability on a special chemical co-operation corresponding to the consortium character; *i.e.*, to the fact that these plants are a symbiotic association of an alga and a fungus living by a kind of mild parasitism—the fungus borrowing from the alga its carbohydrates, while the alga in return borrows its water, proteids, and salts from the fungus. In the many cases where the lichen acid is an ester, “one may, perhaps,” says Zopf, “so imagine this co-operation that the alga yields the alcohol (*e.g.*, in the form of erythrite), the fungus the acid (in the form of lecanoric acid),” the result being represented by erythrin; the species of *Rocella* which produce this substance carry algæ of the genus *Trentepohlia* which in fact form erythrite. Now, no doubt the acids are the result of the peculiar symbiotic association of alga and fungus, and the latter is the sole seat of the production—actual appearance of the acids (it does not produce these by itself); but the important fact that when the quantity of the albumenoids decreases the quantity of the acid increases points to a more specific origin. The co-operation, in fact, seems clearly to consist in this, that as the alga borrows its albumenoids from the fungus, a powerful process of deassimilation is inevitable in the latter. The alga would imperatively require the nitrogenous groups of the albumenoid molecule, the aromatic groups thereof would not be needed, and would be left behind in the fungus. The acids therefore originate by a mechanism of deassimilation, provoked by a penury of nitrogen in the neighbouring cells of the alga, whose cells, moreover, seem to exist in a kind of juvenile condition as compared with those of the fungus, which are naturally highly nitrogenous with a great reserve of force. This latter circumstance may be connected with the peculiar phenolic chromogens evolved by lichens, *viz.*, orcinol, quinones of the anthracene series. The methylation points to a more extensive abandonment of the carbon groups than is usual in similar processes (production of floral pigment, &c.) taking place in the higher plants.

### *Gallotannin.*

Many of the old analysts seemed to detect this form of tannin and its acid (gallic acid) in a great number of plants; *e.g.*, in nettle, tea, *Euphorbia*, *Coriaria*, various species of geraniums, arnica, plumbago, yellow water-lily, &c. The leaves, bark, &c., of various trees and shrubs were also said to contain gallotannin, such as oak, poplar, birch, hazel, dogwood, &c., and even lately Trimble asserts that the tannin of the Spanish chestnut tree is the same

substance. It may, however, be safely asserted that no tannic derivative of pyrogallol exists in any normal part of the plants mentioned. Among British herbaceous plants I have found it only in members of the orders *Onagraceæ* and *Lythraceæ*. The detection of gallotannin in a plant may be illustrated by the behaviour of the aqueous solution of an alcoholic extract (after benzene) of the over-ground parts of a willow-herb (*Epilobium*), *viz.*, with iron salts a blue-black precipitate, with ammonia a yellow colour with scarlet streaks to a brown-yellow liquid, with lime-water yellow, green, and brown precipitates, with acetate of uranium a brown precipitate; precipitates also with gelatin and tartar emetic plus  $\text{NH}_4\text{Cl}$ , but none with bromine water; when a drop of sulphate of potash solution followed by a few drops iodine solution are added an instantaneous transient red coloration is immediately produced; finally, no phlobaphene was yielded by boiling  $\text{HCl}$ . It is hardly necessary to say that no other kind of tannin or tannoid extracted from plants yields a series of reactions comparable to the above. There are, however, certain tannins which are partially similar thereto in some respects; for instance, those of sedum, bistort, various *Rosaceæ*, dogwood, Spanish chestnut; but all these precipitate bromine water and yield phlobaphenes, and do not give the icidine reaction. All these, moreover, contain catechol and phloroglucin nuclei, and it is probably owing to the fact that the latter is attached to the remainder of the molecule by a single bond, or some phloroglucin hydroxyls are free, that the blue-black reaction with iron salts, which distinguishes these tannins, is obtainable. According to Trimble, the blue colour with iron salts given by oak tannins is due to a foreign substance and never to the pure tannin, but the analogy of the tannin of several *Rosaceæ* (burnet, lady's mantle, blackberry, marsh cinquefoil, common avens, &c.), which also yields blue or blue-black precipitate, would seem to show that it is really caused by some constitutional property of the tannic molecule. According to Winkel, no free phloroglucin or other phenol is ever present in plants—a statement with which I agree—and this fact lends support to the view that the tannins as actually existing in the tissues are really comparatively stable substances.

### *The Origin of Oxalate of Calcium.*

This subject in its physiological bearings (final cause) has proved to be the bone of considerable contention. Originally, oxalate was reckoned to be a reserve substance serving the supply of cellulose material. Some authors deny this and say that it is specially formed in those cells in which mucilaginous substances of a chalky nature or pectin compounds are very copiously accumulated. According to Duclaux, it is the result of an incomplete combustion, and this view seems to be very prevalent. Schimper's renowned theory is that the oxalate is a by-product in the formation of organic phosphates (nuclein, &c.), and its appearance is connected with the reduction of nitrate of calcium in the leaf, the nitrogen of the acid being assimilated, the oxygen thereof being cast on the sugars, and the resulting oxalic acid is deposited as a calcium salt; *i.e.*, oxalate of calcium is formed in order to eliminate oxalic acid. Amar, on the contrary, maintains that it is formed in order to eliminate calcium. It is certain, however, that the results of a comprehensive chemical analysis of plants do not warrant the formulation of any of the above hypotheses. It is certainly not true that plants which specially absorb and utilise the nitrates of the soil are always distinguished by a copious formation of oxalate, *i.e.*, borage, foxglove; while, on the other hand, plants which contain no nitrate, *e.g.*, several *Liliaceæ*, most native forest trees, &c., frequently produce large quantities of oxalate. Similar remarks apply even more forcibly to mucilaginous plants, several of which contain little or none of this salt; *e.g.*, marsh marigold, lesser celandine, valerian, various grasses, &c. It seems to me that the views of MM. Mazé and Ferrier on this subject (*Compte Rendus*, 1904, cxxxix.) are quite correct, *viz.*, that the



vegetable acids are not a product of the direct oxidation of carbohydrates by oxydases or otherwise. In fact, they are produced as a product of deassimilation, and not in connection with assimilation, as Schimper assumed. The respiratory combustion supposed to form the acids is exerted upon the living protoplasm itself as an organic process, the acids being, in certain circumstances, detached from the albumenoid molecule. In some leaves, such as elm and sycamore, for instance, where the total nitrogen as well as the sugar and mucilage do not decrease till very late, as well as in other leaves (cherry and birch) where the same constituents do decrease, there is about an equally heavy deposit of oxalate in the old organ, thuswise exhibiting, as regards its formation, an independence of carbohydrate.

#### *The Chromogen of the Gentian Blue.*

One would imagine that this subject would be one of entrancing interest to all students of botanical chemistry, but I am not aware of any European publication, paper, or memoir dealing specially with the chromogen of the noblest of Alpine flowers. Of fifty-nine species of *Gentiana* thirty-five are blue, and there is no pink. Independently of the very favourable physiological or anatomical characters (the huge and rapid development of the corolla, the large pollen grains, the extremely numerous ovules, &c.), there must inevitably be something specially potent in the chromogen which ministers to the evolution of the intense blue coloration of the floral envelope. Unfortunately, so far as I am aware, there is no tannin, strictly so-called, produced in any of the gentians which are readily available for examination. There is, however, a tannoid which seems to be characteristic of the Gentianodes division of the order, and is named gentsin,  $C_{14}H_{10}O_5$ , is a member of the xanthone group of natural dye-stuffs, and contains the quinol and phloroglucol nuclei or residues. It would seem that it is to the quinol nucleus or complex that the blue coloration of the gentian corolla is mainly attributable, and this statement will seem justified by the following facts:—On an analysis of the leaves of a plant, the bogbean (*Menyanthes trifoliata*) belonging to the order *Gentianaceae*, I was extremely interested to find (the fact had never been recorded before, I believe) that they contained caffeetannin, and I forthwith concluded, rightly I hope, that this was the actual tannic chromogen of the gentian blue. It may be mentioned that all the allied orders (*Oleaceae*, *Apocynaceae*, *Asclepiadeae*, *Aquifoliaceae*) contain a quinol tannin, and all exhibit blue flowers in many of their species, and these blues, be it observed, are true blues, and not purples or violets as in *Leguminosae*, *Geraniaceae*, &c., Caffeetannin is a substance that has proved a puzzle. Some chemists hold that it is a sugary diether of caffeic acid, and others say that it is not a glucoside, and yet one or two affirm that it is a mere mixture of acids and other substances. What is certainly true is that it yields proto-catechuic acid on fusion with potash, and that its reactions are not similar to the ordinary catechol tannins, the latter fact being a conclusive proof that it contains in its molecule a nucleus other than that of catechol or phloroglucol. This other nucleus is evidently quinol, although caffeic acid is considered to be a derivative of styrene, which is a side-chain derivative of benzene. In fact, free cinnamic acid has been found in various labiates, figwort, &c., which contain caffeetannin or ferulic acid, and, as is known, *Salvia patens* is one of the most distinct and beautiful deep blue flowers in cultivation. All tannins possess a chromogenic nucleus of a phenolic nature upon which an aldehyde in a favourable acid medium reacts to produce a coloration, and it is very important to notice that caffeetannin is the only tannin known, besides gallotannin, which yields oxidative blue compounds with bases. Moreover, these tannins contain more HO groups in their molecule than any other. According to Liebermann the entrance of HO groups (both as to number and position) into a colouring matter changes the tint from yellow up to blue, and finally black. The state of the question here

discussed seems therefore to be this. Caffeetannin (considered as the gentian chromogen) contains no less than six HO groups according to Gortler, and hence there is a greater possibility, and, under the prevailing physiological conditions, a greater probability, that some of these groups will settle into a position capable of producing a brilliant, potent, and true blue pigment in the corolla.

Patterdale, Westmorland.

### THE PRODUCTION OF FORMIC AND ACETIC ACIDS BY THE ATMOSPHERIC OXIDATION OF TURPENTINE.\*

By C. T. KINGZETT, F.I.C., F.C.S.,  
and  
R. C. WOODCOCK, F.I.C., F.C.S.

AMERICAN turpentine, pinene prepared from American turpentine, Russian turpentine, and sylvestrene prepared from Russian turpentine, were respectively mixed with their own volume of water and oxidised by a current of air at 65° C. for twenty-four hours. The aqueous solutions were then examined, and gave the following results:—

*American Turpentine.*—Formic acid, 0.017 per cent; acetic acid, 0.038 per cent; formaldehyde, indications; acetaldehyde, none.

*Pinene.*—Formic acid, 0.14 per cent; acetic acid, 0.057 per cent; formaldehyde, indications; acetaldehyde, none.

*Russian Turpentine.*—Formic acid, 0.026 per cent; acetic acid, 0.108 per cent; formaldehyde, indications; acetaldehyde, none.

*Sylvestrene.*—Formic acid, 0.16 per cent; acetic acid, 0.086 per cent; formaldehyde, indications; acetaldehyde, none.

As might be expected, acetaldehyde was not found owing to the ready oxidation of that substance into acetic acid; possibly, however, acetaldehyde and formaldehyde are formed intermediately, the two substances being converted into the corresponding acids by subsequent oxidation.

American turpentine, pinene, Russian turpentine, and sylvestrene were dried over ignited calcium chloride, and then oxidised with a current of dry air at 65° to 69° C. during a period of some weeks, when the oils had the following specific gravities:—American turpentine, 931; pinene, 962; Russian turpentine, 940; and sylvestrene, 958. The oxidised oils were shaken up with half their volumes of water, and the aqueous solutions examined, with the following results:—

*American Turpentine.*—Formic acid, 0.055 per cent; acetic acid, 0.024 per cent; formaldehyde, none; peroxide of hydrogen, 0.71 vol.

*Pinene.*—Formic acid, 0.054 per cent; acetic acid, 0.186 per cent; formaldehyde, indications; peroxide of hydrogen, 0.348 vol.

*Russian Turpentine.*—Formic acid, 0.13 per cent; acetic acid, 0.08 per cent; formaldehyde none; peroxide of hydrogen, 1.06 vol.

*Sylvestrene.*—Formic acid, 0.059 per cent; acetic acid, 0.264 per cent; formaldehyde, indications; peroxide of hydrogen, 0.532 vol.

With respect to the two samples of turpentine, the air after passing through the turpentine was washed in a flask of water. This water was found to contain considerable quantities of formic and acetic acids, also peroxide of hydrogen, but only indications of formaldehyde. Peroxide of hydrogen when added to American and Russian turpentine produces some formic and acetic acids, but the action is slow.

\* A Communication from the Laboratories of the "Sanitas" Co., Ltd. Read before the Society of Chemical Industry, January 8, 1912.

Formaldehyde yields formic acid when treated with peroxide of hydrogen. When acetaldehyde and formaldehyde are added to a mixture of water and turpentine and subjected to a current of air, the aldehydes are oxidised in course of time into the corresponding acids.

When dried Russian turpentine is oxidised by dry air and the volatile portions condensed, a small quantity of oil is obtained, which on being shaken with water yields peroxide of hydrogen, formic and acetic acids, thus proving that some part of the active peroxide formed by the oxidation of the turpentine in the dry state is carried over as vapour. Water is also produced when dry turpentine is oxidised with dry air, thus indicating a splitting up of the terpene molecule. The interpretation of the results obtained is still left in some doubt, for it is not yet definitely ascertained whether the  $H_2O_2$ , the formic acid, and the acetic acid severally depend for their production upon the interaction of water on one organic peroxide or more than one, and whether or not the two acids result from the oxidation of formaldehyde and acetaldehyde as produced in association with the said organic peroxide or peroxides. It is not probable that the formic and acetic acids result entirely from the subsequent action of the peroxide of hydrogen (first produced) on the terpene molecule in view of the results obtained. We favour the view that one organic peroxide alone is formed, and at the same time either acetic and formic acids or acetaldehyde and formaldehyde, the two latter substances being resolved into their corresponding acids when the organic peroxide yields peroxide of hydrogen, as it does on being placed in contact with water.

## A MODIFIED GOOCH FILTER.

By W. R. FORBES, B.Sc.

THIS form is very useful for quick filtration. It has one disadvantage in that, unless much expense is incurred, one must use the same size "Gooch" each time. At times a large or a smaller one would be an advantage. It is thought that by the following modification this aim can be attained.

Instead of the usual washer which lies between the "Gooch" and the glass an india-rubber tyre would be used. This tyre would surround the "Gooch," and could be inflated to fill the space between the "Gooch" and the glass. A side tube (with a clip) to the tyre would be needed to inflate and disinflate it.

By this means one could use a larger or smaller "Gooch" as one pleased.

## CHEMICAL ENERGY.\*

By J. E. MILLS.

(Concluded from p. 21).

### Conclusions Suggested Regarding Chemical Energy.

THE study of chemical energy as set forth in this paper has covered but a small portion of the field. The electron theory, the valency theory of Barlow and Pope (*Journ. Chem. Soc.*, 1906, lxxxix., 1675; 1907, xci., 1150), the work of Traube upon atomic volumes, of T. W. Richards ("The Compressibilities of the Elements and their Periodic Relations," *Proc. Am. Acad.*, 1901, xxxvii., pp. 3, 399; 1902, xxxviii., 293; 1904, xxxix., 581) upon the compressibility of the elements and the relations of volume to chemical energy, and of Werner (*Ber.*, 1907, xl., 15, and numerous other

papers) upon the conductivity and valency relations of certain classes of organic compounds, all constitute recent notable advances in our knowledge of chemical force and its action. I make no attempt to consider the entire field. In my own study of molecular and chemical attraction I have been most forcibly impressed by the possible truth of three ideas:—

*First.*—That the attractive forces, whatever their nature, whether chemical, molecular, magnetic, electrical, or gravitational, which proceed from a particle are definite in amount. If this attraction is exerted upon another particle the amount of the attraction remaining to be exerted upon other particles is diminished by an exactly equivalent amount.

*Second.*—In the general resemblance between all of the attractive forces as shown by the accompanying summary.

This table I have given, and to some extent discussed in a previous paper (*Journ. Phys. Chem.*, 1907, xi., 157), and I have there suggested that possibly all of the attractive forces in reality obey the same law, and that the apparent exceptions are caused by our incomplete knowledge of the facts and a misunderstanding of their true relationship. Thus Newton thought that molecular attraction could not be explained as due to gravitational attraction acting between the extremely small molecular distances, because the gravitational force was by no means great enough to account for the molecular cohesion observed, and because the molecular cohesion diminished too rapidly with the distance apart of the molecules. Yet as evidence against this view the author has shown (*Journ. Phys. Chem.*, 1907, xi., 145) that the equation deduced by Helmholtz to represent the energy given out by the sun on contraction under the influence of gravitation, can be used to accurately calculate the energy given out by a substance in changing from the gaseous to the liquid condition, provided only that the constant of Helmholtz's equation be changed.

Newton did not consider that the total available attraction of a molecule was diminished by its attraction for other molecules. In effect Newton's idea makes both molecular and gravitational attraction infinite in amount, or at least capable of infinite multiplication by the introduction of new particles. If the attractive forces proceeding from a particle are definite in amount, then it is possible, I think, that the molecular attraction is merely the residual chemical attraction, and gravitational attraction is the residual molecular attraction. Magnetic force is possibly a manifestation of molecular attraction, and electrical force is possibly identical with chemical force.

In the paper cited above, we have discussed this idea somewhat more in detail, and have there suggested that possibly all of the attractive forces could be measured by—

$$\frac{\text{Amount of attraction neutralised at unit distance}}{d^2} \times \frac{\text{Amount of attraction neutralised at unit distance}}{d^2}$$

where  $d$  is the distance apart of the attracting particles.

The view which we have expressed above enables us to obtain a very clear idea of the theoretical significance of temperature and the absolute zero. If the atoms of a substance be supposed at an infinite distance apart, the total energy possessed by an atom may be of two kinds. First, the potential energy of its own attractive force, and second, a possible energy of translational motion. This latter motion, under the conditions named, would be a measure of the temperature of the body. Now as the atoms move closer together, the potential energy of attraction is partially transformed into translational motion, but this additional motion of the atoms so gained is not entirely motion which constitutes temperature. Of the total gain of kinetic energy caused by the attraction some must be retained for stable equilibrium under the conditions, as a balance, as it were, for the attractive force. (The amount so retained can be calculated, where the law of the force is known, for the simplest case of two particles). Only the excess of energy above this retained amount becomes visible as temperature.

\* A Paper read at the Fourteenth General Meeting of the American Electrochemical Society.

† Numerous papers. Among others, his "Grundriss d. Phys. Chemie"; Boltzmann, "Festschrift," 1904; *Zeit. Anorg. Chem.*, 1904, xl., 380; Sammlung, *Chemischer und Chemische-technischer Vorträge*, iv., 255; *Ber.*, 1907, xl., pp. 130, 723, 734, 2341.



| Force.        | Medium of propagation. | Effect of temperature. | Is the attraction neutralised? | Is the attraction directive? | Law of distance, $d$ . | Numerator          | Factor of Force.            |
|---------------|------------------------|------------------------|--------------------------------|------------------------------|------------------------|--------------------|-----------------------------|
| Chemical ..   | Ether                  | No effect              | Neutralised                    | Yes                          | ?                      | Nature of atom     | $\times$ Nature of atom     |
| Molecular ..  | Ether                  | No effect              | Neutralised                    | ?                            | $1/d^2$                | Nature of molecule | $\times$ Nature of molecule |
| Magnetic ..   | Ether                  | ?                      | Neutralised                    | Yes                          | $1/d^2$                | Strength of pole   | $\times$ Strength of pole   |
| Electrical .. | Ether                  | ?                      | Neutralised                    | Yes                          | $1/d^2$                | Charge             | $\times$ Charge             |
| Gravitational | Ether                  | No effect              | Not neutralised                | No                           | $1/d^2$                | Mass               | $\times$ Mass               |

The temperature motion is the excess of translational motion impressed upon an atom or molecule beyond that which it would retain as a necessary attachment of its potential energy under the conditions considered

Thus at  $-273^\circ\text{C}$ . we undoubtedly, I think, have atomic motion, and might have molecular motion, but to my mind at least the extreme theoretical and practical importance of that point as the "absolute zero of temperature" is not decreased thereby.

*Third.*—Regarding more particularly the relationship between electrical and chemical forces, I have in my own mind connected the power to conduct electricity, whether the substance is in the solid, liquid, or gaseous condition, not primarily with molecules, nor with ions, nor even perhaps with electrons. The essential requisite appears to me to be a free; that is, an unabsorbed attraction. My meaning will become clear by a brief discussion.

The best conductors in the solid condition are the metals such as copper, silver, platinum, &c., and these metals are monatomic. That is to say, the chemical attraction which the atoms of these metals possess is not bound hard and fast to another atom, a mutual absorption of the attraction between the two atoms having taken place. The attraction is, indeed, to some extent absorbed by the neighbouring atoms, for I think there is no very clear distinction to be drawn between molecular and chemical attraction, but the attraction is so distributed that it is easily loosened and becomes free. In the metals which conduct less well, such as bismuth or antimony, the atoms, as is well known, are partly combined, and the attraction is therefore more difficult to free, and it becomes more difficult to propagate the attractive wave. Our best insulators are the most stable chemical compounds, glass, clay, oxides, salts, &c., or compounds such as rubber, where the chemical attraction of the atoms is almost completely saturated by other definite atoms. If these bodies are to conduct electricity the stable chemical union must be broken down, or at least loosened. This loosening of the chemical union happens usually with an increase of temperature.

A stable gas, such as oxygen or hydrogen, is a poor conductor. If such a gas is to be made a conductor it must be "ionised"; that is, the chemical attraction which before was definitely absorbed by some other atom must be made free.

Considering solutions, an acid, base, or salt, when dissolved in water becomes a good conductor, because, using sodium chloride as an illustration, the condition in the solid is represented by a sodium atom and a chlorine atom which mutually saturate each other's attraction. As a dissolved salt, the sodium attraction is partially or wholly loosened from the chlorine, and this attraction distributes itself upon the hydroxyl portions of the neighbouring water molecules. The attraction of the chlorine for the sodium is, of course, loosened at the same time, and distributes itself upon the hydrogen of the neighbouring molecules. Whether the water molecules and the sodium chloride molecules are definitely pulled apart I do not know, but the facts of the electrolytic dissociation theory form partial evidence that they are. In the case of acids, bases, and salts, the breaking apart of the dissolved molecule is possibly complete at "infinite dilution." In other cases the dissolved substance retains its chemical identity, and this means nothing else than that the mutual atomic attractions remain definitely bound, and the substance remains a poor conductor.

Unless a distributed chemical affinity is equivalent to an electrical charge I see no reason for supposing that "ions" have electrical charges. Otherwise I think that the electrolytic dissociation theory represents an essential part of the truth. But no less essential is the point so repeatedly emphasised by Kahlenberg, that there is a union between the solvent and the dissolved substance. We believe this union to be stronger or more complete the more completely "dissociated" is the dissolved substance. The hydrate theory, the dragging of the solvent molecules by the ions, and the change in concentration around the electrodes, bear decidedly upon this point. Kohlrausch advances essentially the same idea (*Proc. Roy. Soc.*, 1903, lxxi., 338), and it is further discussed and supported by Bousfield (*Zeit. Phys. Chem.*, 1905, liii., 257). Lewis (*Journ. Am. Chem. Soc.*, 1906, xxviii., 906), in his review of recent advances in physical chemistry, says:—"In many investigations it has been shown that the solutes which give conducting solutions are able to form definite solid compounds with the solvent, thus indicating that in the solution, too, there is a union of solvent and solute."

We have only extended these ideas a little by saying that atoms whose lines of force radiate out indiscriminately to other atoms are good conductors. Atoms whose lines of attractive force extend to certain other definite atoms, the attraction of each being mutually saturated thereby, are very poor conductors.

## ALLOYS.

By W. R. WHITNEY.\*

THIS is not intended as a paper describing accomplishments, but is aimed at contributing, if possible, to increase the interest of experimenters in new alloys. It is the result of reading Mr. Stephenson's paper on "The Value of the Association to its Members," and a letter from the secretary, asking for a contribution to the papers of the American Brass Founders' Association.

I want to call attention to the possibilities in the way of useful discoveries, which may well lie more nearly within reach of some of the members than they realise, because of their particular knowledge or possession of special materials. For example, it frequently happens that one manufacturing company produces a new metal or alloy for some particular use, which, owing to lack of general study, may remain the sole use for a long period of time. Probably those who produce the special cerium-lanthanum-iron alloy used in the various types of friction cigar lighters have not been able to study very thoroughly the application of this alloy to other uses. So also, those who use the very modern metals, tantalum, tungsten, and molybdenum, have been engrossed with applications to a single field, and have hardly been able to look carefully into others. It is often through the interchange of information across the gap between quite remote fields that useful advances are made.

It occurred to me that even an imperfect review of some of the relatively recent metals might not come amiss. Probably few realise the rapidity with which new metals are coming into use, particularly in alloys. There are in all approximately 50 metallic elements, though most of our

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important industries employ but a few of them. Some of these, in the metallic state, have market prices which are not yet controlled by the cost of production, nor by the infrequency of occurrence, but rather by the lack of development of a utility. Beginning with gold, which we may assume is the one element whose exchange value depends upon its commonness in nature plus its cost of production; and passing over iron, copper, lead, and zinc, whose values may be said to be well fixed by occurrence and costs of production, we soon reach other metals, for which a new demand might well greatly reduce the cost. Among these are many whose ores occur in abundance. In the case of this type of element the interest attached to research work is doubly great.

It is highly improbable that the cost of copper will ever be greatly changed by the discovery of new uses. This is because the world's supply of the ore is pretty well known; the demands are high, and the cost of production of metal from ore have been so studied that further reduction will probably only be of what I like to call the second order of magnitude. This was not true of the metal aluminium a few years ago, and it is still possible that considerably wider uses and reduction of production costs may develop in its future. There is apparently a much wider divergence between the occurrence of the aluminium in nature and its price in metallic state than in the case of copper. In case of aluminium, only selected and purified ores are used at present, while other compounds of it occur everywhere in nature. On the other hand, in the case of copper, ores containing even less than 2 per cent of copper are worked for the metal. Aluminium may thus still be considered in the transition state, a state long ago passed by copper and iron, and not reached by some of the metals considered below. We have all been witnesses of the interesting advance of aluminium. From 1869-74 its properties were becoming generally known. The inefficient process by which it was then reduced from its ores made it impossible to sell the metal below 10 dols. per pound. Advance was then made so that in the 80's the price was about 5 dols. There was not a great demand for it at this price. In the year 1907 something like 26,000,000 lbs. of this metal were made in America alone. The price is now about 20 cents per pound.

The element calcium, which a few years ago was listed only as museum specimens and at several dollars per grm., was sold in 1908 at 1.50 dols. per pound, and could certainly be sold for a small part of this price if a greater use could be found for the metal. It slowly decomposes water, giving hydrogen, and it differs from the alkali metals in producing such a feeble alkaline solution that it is generally harmless. It ought to serve as a good deoxidiser, and should be a very cheap metal. It is not fair to relegate it to a list of useless metals. History of the metallic arts points to there being no such list.

*Thallium* is an element quite similar to lead, but probably possessing some property which will some day warrant its exploitation. It is softer and heavier, and could be obtained in quantity if a demand were created.

The elements *chromium*, *molybdenum*, *tungsten*, and *tantalum*, the three latter now obtainable in wire-form, are tempting elements to study in mixtures with others. Who knows the useful properties of a chromium bronze, for example?

*Tellurium* has long been an apparently useless metal, and any market price is fictitious, as there is but little isolated in metallic state. It is not necessary that a great use, such as a substitute for zinc in brass, should be found for it. Our industries are so great, that if a pound of tellurium added to the ton of aluminium was of benefit to the latter, the production of the necessary tellurium would be real industry.

Consider *cobalt* a moment. The world's rate of supply of ore has been greatly augmented. It may take time to actually realise a greatly reduced cost of metallic cobalt, but we ought, notwithstanding, to realise it when uses have been developed. Our natural impulse in such a case

is to try direct substitution of one metal for another in some well developed use. Cobalt, for example, might replace nickel in most uses when the cost fell below that of nickel, but this is a second order use. A first order use would be the supplying of a want which no metal previously supplied, or supplied distinctly less perfectly.

In this connection an interesting alloy of cobalt and chromium has just been described by Elwood Haynes in the October number of the *Journal of Industrial and Chemical Engineering*, and it is altogether probable that technical use will soon be made of it.

Many tons of metals are annually consumed as resistance wire for electrical purposes. At one time iron was the element most used. German silver replaced it in some cases, where a lower temperature coefficient was needed and the increased cost was permissible. Now there are a dozen or more special alloys for this particular electrical use. The new ones have far out-classed the old in most of those properties for which the electrical engineer uses them. In such alloys, nickel, chromium, manganese, and others are now used by the ton.

*Silicon*, which in 1900 was a curiosity and sold for 40 cents per grm., is now a necessary component of special iron alloys and of high-grade transformer iron, and the world uses thousands of tons of the alloy annually. Silicon is now sold at about 5 cents per pound. The use of this metal in other alloys is still quite limited. In the case of iron it greatly decreases hysteresis loss and increases electrical resistance.

*Boron*, still a quite expensive material in metallic state, is coming into commercial use in assisting the making of solid copper castings of high electrical conductivity.

*Vanadium* seems to be a young wonder working metal. Its use has increased very rapidly in the past few years, but the quantities consumed are not known to us. As several companies are producing the iron alloy, it is safe to assume that it is being sold by the ton. The price for the metal in the alloy is not far from 5.00 dols. per pound.

*Cadmium* is a beautiful metal in many respects, and it is certainly awaiting use. It is whiter and less crystalline than zinc, and doubtless the high price of nearly a dollar a pound keeps practical workers from trying it in their experiments. It should be produced as cheaply as aluminium, if there were a good demand for it.

*Titanium* is an element long the subject of criminal negligence. It is a high-melting ductile white metal, which, at present, is only separable from its ores at high cost. It exists in many cheap ores widely distributed in nature. It is now apparently coming into use in steel manufacture, particularly for railroad rails, and for this purpose it is fortunately unnecessary to isolate the pure titanium from its ores, an iron titanium alloy being produced directly. What will happen when the pure element has been tried in special fields can only be surmised. The optimist sees great chances. The pessimist feels himself busy living with the optimist.

If one omits the common alloys, brass, bronze, solder, &c., and considers only possible alloys of two metals, and still confines himself to twenty of the common metals, like vanadium, manganese, chromium, boron, &c., he is interested at once to recognise that there must be one hundred and ninety different pairs of binary alloys. When, in addition, the effect of varying proportions in these alloys is considered, it becomes evident that the field of alloy-research is truly a large one. Many of the alloys apparently unstudied are those which melt at extremely high temperatures.

The brass founder who knows the upper limiting temperature of his melting furnaces may at once point out that this temperature is fixed both by the life of crucibles and the particular coke or oil-heating schemes with which he is familiar. If he thought that a molybdenum bronze of 80 per cent molybdenum would have useful properties compared with all other alloys, he might at once conclude that he must give up his alloy because of the difficulty of melting

it. If it were not for the advances in our available temperatures, there would seem to be little more than amusement in considering alloys high in tantalum, in chromium, in titanium, in molybdenum, in silicon, in uranium, in vanadium, and a number of other high-melting metals, but hand in hand with the discoveries leading to isolation of such metals go also discoveries of aluminothermics, oxyacetylene and oxyhydrogen temperatures, and electric furnace processes. The time is always ripe for the study of new alloys with new tensile strengths, elasticities, colours, and wearing powers. The automobile and the aeroplane have forced the aluminium and iron alloys to make rapid strides, and it is natural that we should want to inventory our possibilities. The physical chemist has started along the way of a systematic co-ordination of certain properties of binary, and in a few cases tertiary alloys. He has shown how to plot a few freezing points of two-metal and three-metal mixtures, and to construct therefrom curves showing not only all possible alloys, but what may be expected in the way of segregation and structure and such effects as caused by annealing or quenching.

He has found that there is a solubility of metals in one another which varies just about as the solubility of substances in water varies. Metals may be melted together and well mixed, but the quality and permanency of the mixture is determined by just such solubility laws as control ordinary solutions. We know that in some cases well-mixed melted metals will separate into two layers if allowed to remain even a few moments in molten condition at low temperatures. They act like a mixture of water and ether. The two separated layers contain both metals, no matter what the temperature, but the quantitative compositions depend on the temperature.

The other extreme of metal solubility is found in such a case as zinc-cadmium, which acts much like a mixture of alcohol and water, the two components going into solution in all proportions and remaining in solution at all temperatures. Having seen this analogy between the facts of solubility of substances in water, it is natural to search among the metal mixtures for all the peculiar kinds of solution observed in aqueous solutions. Two such classes interest us at once. They are those corresponding to aqueous solubilities where temperature widely influences the quantities dissolved, and those in which the solvent (as water) combines with the dissolved substance more intimately than by simple solutions, as by chemical combination. In the case of zinc and lead we have one of the metal alloys of limited solubility. If these two metals are well mixed in liquid state they separate into layers—one, the zinc, carrying a few per cent of dissolved lead floats on an alloy made up of lead carrying a few per cent of dissolved zinc. In general, the quantity of the one metal dissolved and held in solution by the other depends on the temperature, and the higher the temperature the greater the solubility. Between 900° and 1000° C. they are apparently completely soluble. It follows from this that when a dissolved pair of metals is cooled slowly, one of them may separate on cooling if the limiting solubility is reached, and the extent of effective separation may depend on the rate of cooling.

Our second case, that of chemical combination between the metals, is made most evident by the form of the freezing-point curve of the possible alloys. A compound of two metals which is stable at a temperature above the melting-point of one or both of the metals shows very clearly on the melting-point curve, and acts towards each of the elements just as a new or third element. Its melting-point cannot yet be predicted from any knowledge of the component metals. It may even melt higher than either of the components. Such cases are seen in alloys of aluminium-antimony, in lead-tellurium, &c.

Man first used the metals as he found them; then, as he reduced them from the ores, and finally, when specified requirements became more and more exacting, he not only brought into use previously unused metals, but also greatly

modified the old familiar ones. For a harder iron he used steel, a carbon alloy; for a harder steel, or one capable of cutting iron more readily, he added tungsten, nickel, chromium, and other metals. For permanent magnets molybdenum was added; for high electrical resistance nickel, chromium, &c., were added; for low electrical resistance and low hysteresis silicon and aluminium were added; for toughness in springs a little vanadium was used, and for wearing qualities titanium is now introduced. These are only a few of the successful alloying experiments with iron. They will probably be repeated with other metals, such as copper, zinc, and aluminium, where the cost of the base metal is not high.

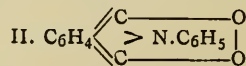
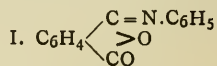
On the other hand, the study of those metals which have not yet advanced to a stage where first order cost-reduction is impossible is equally interesting. Consider again the element chromium. What do we know about it? Is it a workable metal? Can it be hammered or cast? Is it permanent in the air? Is there a considerable possible ore supply? Has the cost of obtaining the metal been reduced to what seems a reasonable rate? &c., &c. As it is unlikely that such an element will suggest itself for use by men as did copper and iron, it is probable that its properties must first be determined and made known. As a metal it is only about fifteen years old. It is made in the metallic state by reduction of the oxide by metallic aluminium, and also by electrolysis of its salt solutions. It cannot yet be produced at a lower cost than that of the aluminium required, and it now sells at about 80 cents per pound. In the oxide from which it was made it may be had for less than half this cost, and in its alloys with iron, which are made by direct reduction with carbon, it is sold for 29 cents per pound. This gives a rough idea that ultimately, by perfection of metallurgical processes, &c., we may possibly obtain the metal much below 80 cents per pound. It withstands heat exceedingly well. When pure it melts at very high temperature (Ostwald, about 3000° C.), and it does not scale when heated red hot in air as copper and iron do. It is for this reason that it is used in resistance alloys for electric heating devices. It has been plated on to metals, and then looks and acts like nickel plate. Doubtless its use will quite rapidly increase in special alloys, as it has already come into use in tool steel.—*The Chemical Engineer*, xiv., No. 4.

## ISOMERIC PHENYLPHTHALIMIDES AND SOME ALLIED COMPOUNDS.\*

### II.

By MITSURU KUHARA and SHIGERU KOMATSU.

In the authors' previous article (*Memoirs of the College of Science*, &c., i., 391) it was shown that two isomers of phenylphthalimide are simultaneously formed instead of phthalophenylisimide, from phenylphthalamic acid by the action of acetyl chloride. Of those two isomers thus formed, one consists of fine colourless needles melting at 83–84°, and the other of light yellow rhombic crystals possessing the melting-point of 125–126°. The authors have designated the former as  $\beta$ -phenylphthalimide, whose constitution has been considered to be probable to stand in agreement with the following Formula I., and assigned Formula II. to the latter for its probable constitution, based upon some analogies which seem to exist between its properties and those of phthalyl superoxide:—



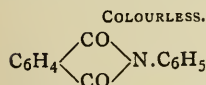
Nevertheless, the authors have been led to the assumption that the latter compound, that is, one which is yellow

\* *Memoirs of the College of Science and Engineering, Kyoto Imperial University*, ii., No. 12.

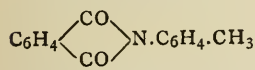


and melts at 125—126°, should be the real unsymmetrical phenylphthalimide, its constitution being preferably represented by Formula I. The reason is as follows:—It is now almost universally accepted that the group  $>C=N-$  is a trivalent unsymmetrical chromophore whose action is rendered conspicuous, especially in the aromatic series, and that its chromophoric character is highly strengthened when an aromatic residue is linked to the nitrogen of the group (see H. Kauffmann, "Ueber den Zusammenhang zwischen Farbe und Constitution bei Chemischen Verbindungen," *Ber.*, xxvii., 3317; xxxi., 2250). On referring to the literatures concerning the compounds which are recognised to contain the group  $>C=N.Ar$ , such as  $>C=N.C_6H_5$ ,  $>C=N.C_6H_4R'$ ,  $>C=N.C_6H_4X$ , &c. (*Ber.*, xiii., 420; xxi., 1415; xxiv., 3518, 3522; xxv., 2056; xxvi., 2292; xxviii., 58, 74, 1120; xxxii., 1678; xlii., 4018; *Ann. der Chem.*, clxxxvii., 199, 215; ccxcv., 31, 90; *Am. Chem. Journ.*, xviii., 813; xxv., 22; *Journ. Chem. Soc.*, lxix., 1212), we always find that they are all coloured particularly yellow or yellowish almost without exception, while the compounds in which an aliphatic residue or hydrogen is linked to the nitrogen are colourless (*Ber.*, xxx., 3006; *Am. Chem. Journ.*, xxx., 26; *Ann. Chim. Phys.*, [6], xxii., 289; *Rec. Trav. Chim.* xii., 22; xiii., 98, 99). Now the authors declare that Formula I., which shows the presence of the chromophoric group  $>C=N.C_6H_5$ , should be applicable to one of the authors' compounds which is yellow, in harmony with the above views. Then, the isomer so called *β*-phenylphthalimide, which is colourless and melts at 83—84°, must possess other constitution different from that ever given, but the authors cannot yet give any satisfactory explanation for the possibility of such an isomer.

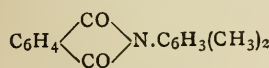
On conducting the experiments for the action of other different aromatic amines, such as orthotoluidine, paratoluidine, *as*-metaxylidine, *v*-orthoxylidine, paraxylidine, and pseudocumidine upon phthalyl chloride, two kinds of isomeric substituted phthalimides, namely, colourless and yellow, similar to those from aniline, were invariably observed to be produced from each amine. The colourless varieties must be the normal compounds of symmetrical constitution like *s*-phenylphthalimide, some such as normal tolyl (*o*- and *p*-) and pseudocumylphthalimides, being already known; but in inferring the constitution of their respective isomers from the view of their coloured nature, the authors assert that they should possess the unsymmetrical structure analogous to *α*-phenylphthalimide, owing to the presence of the chromophoric groups, as will be represented in the following table:—



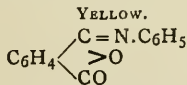
*s*-Phenylphthalimide (known).



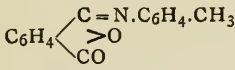
*s*-Orthotolylphthalimide (known).  
*s*-Paratolylphthalimide (known).



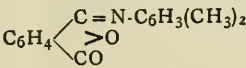
*s-as*-Metaxylphthalimide.  
*s-v*-Orthoxylphthalimide.  
*s*-Paraxylphthalimide.



*α*-Phenylphthalimide.



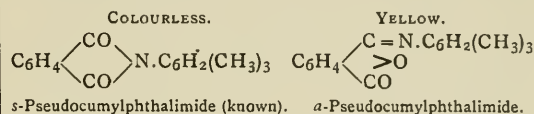
*α*-Orthotolylphthalimide.  
*α*-Paratolylphthalimide.



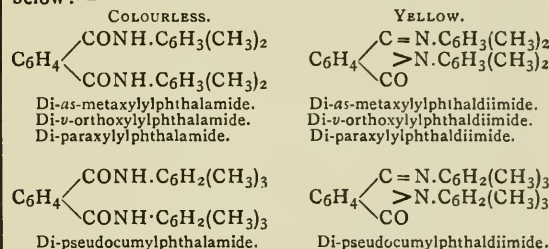
*α-as*-Metaxylphthalimide.  
*α-v*-Orthoxylphthalimide.  
*α*-Paraxylphthalimide.

(NOTE.—Piutti and Abati describe the production of *p*-methoxy- and *p*-ethoxyphenylphthalimides, and *p*-methoxyphenyl- $\Delta_1$ -hydrophthalimide, each in two distinct modifications, yellow and white (of ethoxyphenyl- $\Delta_1$ -hydrophthalimide only yellow form), and ascribe such a phenomena to dimorphism (*Ber.*, xxxvi., 996). The authors, however, are of the opinion that two modifications may be structural isomers, so that the yellow one

would take the asymmetrical structure owing to the presence of a chromophoric group and the white one the symmetrical. Piutti also states the structures of the maleic derivatives of *p*-aminophenol obtained in two forms, yellow and white, assuming the former to take the symmetrical structure, simply based upon the method of the formation of isoidimides (*Rec. Trav. Chim.*, xv., 286), and the latter the symmetrical one (*Journ. Chem. Soc. Abst.*, I., xciv., 783; xcvi., 22; *Chem. Cent.*, 1908, II., 413; 1910, I., 431). The authors dare to put forward an explanation for the structures of two isomers upon the same assumption as above referred, and therefore the representation of the structures of two forms proposed by Piutti should be reversed).



In the case of using xylidines and pseudocumidine there are formed simultaneously, as the reaction products, the substituted phthalimides of the general formula  $C_6H_4(CO.NH.Ar)_2$ , which are readily transformed to the corresponding yellow coloured diimides by the method analogous to that of the formation of von Gerichten's dianil from phenylphthalimide, as previously described in our last article (*Memoirs of the College of Science*, &c., i., 402). while it is strange that with toluidines the analogous compounds could not be obtained at all, although the effort to do so was repeated. The substances thus obtained must therefore be constituted as represented below:—



Moreover, expecting that the Grignard reaction might throw some new light upon the structure of the respective two isomeric arylphthalimides, which it was thought might yield different products, experiments were carefully conducted with different substituted phthalimides and magnesium alkyl haloids.

(To be continued).

## CHEMICAL NATURE OF SOIL ORGANIC MATTER.\*

By OSWALD SCHREINER and EDMUND C. SHOREY.

(Continued from p. 18).

### ACIDS OF UNKNOWN CONSTITUTION.

THERE are a great many chemical compounds, especially of natural origin, to which, while the group to which they belong is well established and their general properties are known, no structure or constitution has been assigned. This is simply another way of stating that all the properties are not known. This meagre knowledge regarding constitution is marked among the higher fatty acids, especially those of infrequent occurrence.

Two acids of this character have been isolated from soils. These acids are isomeric, having the same ele-

\* Bulletin No. 74, U.S. Department of Agriculture, Bureau of Soils

mentary composition, and while one can be regarded as a well-established chemical compound, there is still some doubt whether the other is a single body or a mixture.

#### Paraffinic Acid, $C_{24}H_{48}O_2$ .

The cold alcoholic solution from which  $\alpha$ -hydroxystearic acid has separated in the manner just described is yellow in colour, and evaporation of the alcohol leaves a semi-solid oily mass. On standing some time crystals form in this mass, but the nature of the material was such that they could not be separated without great loss, and so this was not attempted. The oily mass was dissolved again in alcohol and an alcoholic solution of lead acetate added. This gave a yellow precipitate, which was separated by filtration, washed with alcohol, suspended in alcohol, and treated with hydrogen sulphide. After separation from the lead sulphide the alcoholic solution was allowed to evaporate slowly, leaving a somewhat waxy mass of leaflets. This mass was purified by dissolving again in alcohol and repeating the operation of precipitation with lead acetate and finally drying on a porous plate. The body so obtained was light yellow in colour and melted at  $45-48^\circ C$ . Elementary analysis gave the following figures:—

|               | Found. | Calculated for $C_{24}H_{48}O_2$ . |
|---------------|--------|------------------------------------|
| Carbon .. ..  | 78.40  | 78.20                              |
| Hydrogen .. . | 13.29  | 13.00                              |
| Oxygen .. .   | 8.31   | 8.80                               |

This composition, the melting-point, and physical properties correspond with paraffinic acid,  $C_{24}H_{48}O_2$ , described by Pouchet as obtained by the action of fuming nitric acid on paraffin (*Bull. Soc. Chem.*, 1875, xxiii., 111).

The research of Pouchet, on which alone the existence of paraffinic acid rests is, as published, inconclusive as to this body being a definite chemical compound. The quantity of this substance obtained from the soil was insufficient for any extended research, and so far the character of the compound obtained from paraffin has not been studied except that the following facts were established. Paraffin was treated with fuming nitric acid in the manner described by Pouchet and a compound obtained having the properties and composition stated by him. Elementary analysis of this substance gave the following figures:—

|               | Found. | Calculated for $C_{24}H_{48}O_2$ . |
|---------------|--------|------------------------------------|
| Carbon .. ..  | 78.1   | 78.2                               |
| Hydrogen .. . | 13.3   | 13.0                               |
| Oxygen .. .   | 8.6    | 8.8                                |

The properties and composition of this compound corresponded with those of the substance obtained from the soil, and there is little doubt that they are identical. With this understanding the name paraffinic acid is applied to the soil compound. This body has so far been obtained from but one soil, the Elkton silt loam already described. A number of soils have been examined that gave, at the point where paraffinic acid was obtained in the case of the Elkton silt loam, a precipitate with alcoholic lead acetate, but the quantity of material has been either too small for identification or as had other properties and composition.

Very little can be said regarding the possible origin of paraffinic acid in the soil. Several solid hydrocarbons of the paraffin series have been shown to occur in plants, and may therefore be a part of the organic matter added to the soil. Oxidation of these in the soil might give rise to the body found.

It may be noted in this connection that it is well established that paraffin can be oxidised in the laboratory, but usually by rather vigorous treatment. Gill and Mensel (*Zeit. Chem.*, 1869, p. 65) found that on treating paraffin with dilute nitric acid or chromic acid it was oxidised to cerotic acid,  $C_{27}H_{54}O_2$ , acetic acid, and succinic acid. Pouchet in the research referred to found succinic acid in addition to paraffinic acid, but no cerotic acid.

#### Lignoceric Acid, $C_{24}H_{48}O_2$ .

When a soil high in organic matter is carefully heated in a closed tube, there is obtained a dark coloured tarry distillate, which in some cases sets on cooling to a semi-solid crystalline mass.

A peat soil containing 27 per cent organic carbon treated in this way gave a distillate of this character in considerable quantity. The semisolid mass on washing with cold alcohol was freed from much of its colour with little loss of solid matter. The material so washed was completely soluble in hot alcohol, from which it separated on cooling in a bulky microcrystalline form. On repeating this solution and separation several times the material was obtained nearly free of colour. Treatment at this stage with cold petroleum ether removed the remaining colour and a small quantity of oily matter. The body after this purification melted at  $80-81^\circ C$ ., was soluble in ether and hot alcohol, little soluble in cold alcohol, and insoluble in water. Its elementary composition was found to correspond to the formula  $C_{24}H_{48}O_2$ .

|               | Found. | Calculated for $C_{24}H_{48}O_2$ . |
|---------------|--------|------------------------------------|
| Carbon .. ..  | 78.1   | 78.2                               |
| Hydrogen .. . | 13.2   | 13.0                               |
| Oxygen .. .   | 8.7    | 8.8                                |

The compound dissolved in aqueous alkalis, and was set free from such solution unchanged on addition of a mineral acid. The properties, melting-point, and composition indicate the identity of this compound with lignoceric acid first described as obtained by Hell and Hermanns (*Ber.*, 1880, xiii., 1713) from the solid residue or "paraffin" of beechwood tar. It is also found (Krealing, *Ber.*, 1888, xxi., 880) as a glyceride in peanut oil.

It is generally assumed that the lignoceric acid found in wood tar is the result of decomposition effected by the method of treatment, and that it does not occur as such in the wood. In the case of the soil, however, certain observations indicated that this might not be the case. It was observed that if the soil was heated to a high temperature or the heating done rapidly the yield of solid matter in the distillate was very small. When the heating was done carefully, and the temperature raised only to the point where a distillate could be obtained, the solid product seemed to be the result of distillation directly from the soil, and when the operation was carried on in a glass tube such distillation could actually be observed, the melted distillate collecting on the upper cooler side of the tube and being driven forward as heat was applied, just as water would be. It was also found that the purified lignoceric acid obtained from the soil in the manner described could be carefully heating be distilled with little or no decomposition.

With the object of extracting the lignoceric acid from the soil if it existed as such, the soil was treated with boiling 95 per cent alcohol, the extract filtered hot, and allowed to cool. On cooling, a voluminous precipitate separated from the dark coloured extract. This was separated by filtration and purified by dissolving several times in hot alcohol, from which it separated on cooling, and finally by washing with cold petroleum ether. The compound so obtained corresponded in all properties with that obtained by distillation. It melted at  $80-81^\circ C$ ., and elementary analysis gave the following figures:—

|               | Found. | Calculated for $C_{24}H_{48}O_2$ . |
|---------------|--------|------------------------------------|
| Carbon .. ..  | 78.2   | 78.2                               |
| Hydrogen .. . | 13.8   | 13.0                               |
| Oxygen .. .   | 8.0    | 8.8                                |

The identity of the two bodies obtained from the soil by distillation and by extraction with hot alcohol is thus established. It follows that lignoceric acid exists in the soil as such.

Regarding the source of the lignoceric acid in the soil there are two possibilities suggested by our knowledge of the compound. It is, as has been already stated, present in peanut oil as a glyceride, and may be a component of



other vegetable oils and be somewhat widely distributed in plants in small amounts, in which case it might occur in the soil as a residue of the decomposition of such glycerides.

Lignoceric acid is obtained by the distillation of wood, presumably through the decomposition of woody tissue. It is possible that similar decomposition through the agency of micro-organisms may take place in the soil.

#### Resin Acids.

There have been separated from a peaty soil from North Carolina three fractions having the properties of resin acids. While their identity as single chemical compounds has not been established, there is enough known concerning their properties and composition to warrant their description under this division of acids of unknown constitution.

When the alkaline or humus extract of a soil is acidified, the humus extract filtered off, washed, and treated with boiling 95 per cent alcohol, a portion of the humus precipitate goes into solution. If the alcohol is removed by evaporation and water added to keep the volume constant, a dark coloured precipitate is formed, which, after filtration, washing, and drying, is a red or brown resinous powder. This procedure was the preliminary stage in the separation of  $\alpha$ -hydroxystearic acid and paraffinic acid, these being removed from this resinous material by boiling petroleum ether.

The resin acids to be described were obtained from a peaty soil, the same from which lignoceric acid was obtained. The treatment was, as just outlined, the extraction of the humus precipitate with hot alcohol, resulting in a resinous mass which was extracted with petroleum ether. The portion insoluble in petroleum ether, which was the greater portion of the precipitate, was then repeatedly treated with boiling ether until no more material was dissolved. The ether solution was then shaken successively with water solutions of alkaline salts in the following order:—First, 1 per cent ammonium carbonate solution; second, 1 per cent sodium carbonate solution; and finally, 1 per cent sodium hydroxide solution. The extraction with each solution was repeated till no more material was taken from the ether before the next in order was used. This treatment extracted about 90 per cent of the matter originally soluble in the ether. The several alkaline solutions thus obtained were acidified with hydrochloric acid. The resin acids were set free, and being insoluble in water were separated by filtration. They were further purified by dissolving again in ether and repeating the extraction with aqueous solution of the same salts in the same order, the acids being separated, washed, and dried. As so obtained, they were resinous powders varying in colour from light yellow to dark orange. These bodies have been designated for purposes of description, resin acid I., II., and III., I. having been extracted from ether by ammonium carbonate solution, II. by sodium carbonate solution after the extraction of I., and III. by sodium hydroxide solution after the extraction of I. and II. The melting-points of these acids were sharp and were as follows (uncorrected): —I., 100° C.; II., 95° C.; III., 190° C. They had the same general appearance and an indefinite crystalline structure under the microscope. They were readily soluble in alcohol and ether and in aqueous solution of sodium or potassium hydrate; I. and II. were soluble in ammonia, but III. was very slightly so. All gave in alcohol solution a slight reddish colour with ferric chloride, but did not respond to Liebermann's cholesterol reaction.

The elementary composition was found to be as follows, the per cent of ash being given, but the composition stated on an ash-free basis:—

|             | Resin acid I. | Resin acid II. | Resin acid III. |
|-------------|---------------|----------------|-----------------|
| Ash .. ..   | 0.40          | 1.01           | 0.58            |
| Carbon ..   | 68.04         | 73.73          | 74.07           |
| Hydrogen .. | 7.74          | 9.46           | 9.94            |
| Oxygen ..   | 24.22         | 16.81          | 15.99           |

Resin acids II. and III. gave figures so nearly alike that they might be considered identical were it not for the wide difference in melting-point and solubility in ammonia already mentioned. All gave somewhat similar products on fusion with potassium hydrate, a mixture of phenol derivatives, and lower fatty acids.

The method used for the separation of these resin acids is that adopted by Tschirch in the examination of resins. The material left in the ether after shaking with alkalis he designates resin esters. This fraction will be described later. It is evident that in this process there is a separation into fractions that have quite distinct properties and composition in spite of general resemblances. However, the investigation at this stage is quite unsatisfactory in regard to the identity of these several fractions as single organic acids or even as acids at all. It is assumed that because a body goes from solution in ether into solution in an alkaline salt it is a case of a free acid in the ether forming a salt soluble in water. There was, however, in the case of the shaking with carbonates no evolution of carbon dioxide, and the process was not the simple one of a replacement of carbon dioxide and the formation of a salt with the resin acid.

The whole chemistry of the resins and so-called resin acids is in a very unsatisfactory condition. A great many separations have been made similar to those made in this case, named and described as definite compounds, when all that was known was their elementary composition and some of their physical properties.

The class of compounds known as phlobaphanes or anhydrides of tannic acid are closely related to the so-called resin acids in their physical properties, composition, and products formed on fusing with caustic potash. These anhydrides, of which there seems to be a series, adjacent members differing from one another by one molecule of water, are in the same unsatisfactory condition chemically as are the resin acids.

The several members of the phlobaphane series differ in solubility, and any one of the series may change its solubility and other physical properties by losing water and being transformed into another. There is some evidence that in these fractions designated resin acids there is some such anhydride constitution and ready change of solubility.

There is then in the three fractions here described a separation of a considerable portion of the organic matter of a soil into three separate substances having the same general properties but differing in melting-point, composition, and some other properties. No definite conclusion can be stated regarding the identification of these substances, because the chemistry of the natural products to which they are related and with which they must be compared is largely unknown. These fractions form a large proportion of the organic matter, and further research into their constitution and nature is necessary.

Nearly all soils examined give by the method described substances of similar appearance and properties.

#### ESTERS AND ALCOHOLS.

This group finds its largest representation in nature in the oils, fats, and waxes of plant and animal life. Practically all the fats and oils are esters of the alcohol glycerol,  $C_3H_5(OH)_3$ , and may be represented thus:  $C_3H_5(OR)_3$ , where R is the acid radical of a fatty acid. The acid radical may be of one or more acids, but in most natural fats two acids are represented; for instance, oleo-distearin is  $C_3H_5 \begin{smallmatrix} OC_{18}H_{33}O \\ (OC_{18}H_{35}O)_2 \end{smallmatrix}$ . The waxes are usually esters of higher alcohols, such as cetyl,  $C_{16}H_{33}OH$ , ceryl,  $C_{16}H_{51}OH$ , cholesterol,  $C_{26}H_{43}OH$ , with the same higher fatty acids that occur in glycerides. Both oils and fats frequently contain small quantities of the esters classed as waxes. Most of the natural waxes are complex mixtures of esters, higher alcohols, and higher fatty acids, but as in fats and oils the esters are usually the chief component.

From the wide distribution of this class of bodies in plants and animals it follows that considerable quantities of them get into the soil and form the material from which soil organic matter is made. From the evidence at hand in the form of substances isolated from soils, it is clear that in some soils, at least, these compounds persist unchanged. The isolated substances represent esters in the form of glycerides and higher alcohols.

Esters of another class not so well known occur in resins, especially those known as balsam resins. These are generally esters of unknown alcohols with aromatic acids such as benzoic or cinnamic. An ester of this character was separated in connection with the resin acids described in a previous section.

#### Glycerides of Fatty Acids.

When the alcoholic filtrate from the lead precipitate of paraffinic acid obtained in the isolation of this body in the manner described in previous pages is freed from lead by hydrogen sulphide and the alcohol evaporated, there is left an orange-coloured oil which remains clear and liquid at room temperature, but becomes turbid on cooling, crystalline material finally separating. This oil on examination proved to be a mixture of glycerides of fatty acids, as are most natural oils.

The oil obtained in the manner just described is slightly acid to litmus and has an odour not unlike that of olive oil. Its specific gravity at 26° C. is 0.935. On saponification with alcoholic potash and evaporation of the alcohol a soap was obtained completely soluble in water. When this soap solution was acidified with sulphuric acid the fatty acids were set free and extracted by shaking with ether. The mixture of fatty acids obtained on evaporating the ether was a fatty semisolid mass from which crystalline leaflets separated on standing. This mass immediately after removal of the ether had an odour suggesting capric acid, but this disappeared in a short time, leaving a tallow-like odour. On shaking the mixed fatty acids with equal parts of nitrosyl sulphuric acid and water, a solid mass was obtained on standing, thus showing the presence of oleic acid. The original glyceride behaved in the same manner, indicating the presence of oleic acid or olein in the oil. The presence of oleic acid or at least some unsaturated acid was confirmed by the fact that the acid mixture when dissolved in carbon tetrachloride decolorised bromine without setting free hydrobromic acid.

In the water solution left after acidifying the soap solution and extracting with ether the presence of glycerin was shown by the usual tests. The acid liquid was evaporated nearly to dryness and mixed with a small quantity of acid potassium sulphate, and the mass so obtained heated in a test-tube provided with a stopper and delivery tube which dipped beneath the surface of a few cubic centimetres of water in a second tube. The presence of acrolein in the second tube, as a result of the distillation of glycerin, was established by the characteristic odour and by the generation of a pink colour when treated with fuchsine aldehyde reagent. (A solution of fuchsine decolorised with sulphur dioxide).

The fact, then, that the oil obtained from the soil is a glyceride is established, first, by the changed character of the material after saponification, and, second, by the presence of glycerin in the saponification products. It is, of course, possible that there is some free acid present in the oil, but the indications are that such must be small, if any. That the oil is a mixed glyceride is established by the complex character of the fatty acids obtained on saponification, a semisolid mass from which crystalline material separated, oleic acid also being present.

When the soap solution resulting from the saponification of this oil is dried and extracted with petroleum ether, and the ether evaporated, there is obtained a small quantity of unsaponified material. This forms a soft waxlike mass insoluble in water, but soluble in soap solution. This material gave the Liebermann's cholesterol reaction

strongly, but it was not possible to obtain from it any definite crystals of any cholesterol body.

The oil obtained from the soil is therefore a glyceride of fatty acids containing a small quantity of unsaponifiable material, and possibly a small quantity of free acid. As such, then, it corresponds in all particulars with natural glycerides, especially the vegetable oils.

The presence of glycerides similar to natural oils in the soil can perhaps best be explained on the ground that they are unchanged plant residues which have resisted decomposition. Nearly all plants at some stage of their development contain glycerides, and they may also be built up by micro-organisms as with other plants. They are probably not formed by purely chemical reactions such as are likely to take place in the soil.

The presence of unchanged plant glycerides in the soil is of interest in view of the number of bodies of a fatty nature which have already been isolated from soils. In discussing the possible origin of dihydroxystearic acid in the soil, it was pointed out that oleic acid in the form of a glyceride was a nearly universal plant constituent, and that it was possible that dihydroxystearic acid might be formed from it in the soil in somewhat the same way as in the laboratory (*Bull.* 53, Bureau of Soils, U.S. Dept. Agr., 1909; *Journ. Am. Chem. Soc.*, 1908, xxx., 1599). Cholesterol-like bodies seem to occur frequently in soils (*Journ. Am. Chem. Soc.*, 1909, xxxi., 116), and oleic acid or olein may have some relation to the occurrence of this group, inasmuch as Lifschütz (*Zeit. Physiol. Chem.*, 1908, lv., 1) has shown that cholesterol bodies may be formed by the oxidation of oleic acid.

The glyceride just described was obtained from the Elkton silt loam as the final step in the treatment which resulted in the isolation of  $\alpha$ -hydroxystearic acid and paraffinic acid. So far all soils examined in this manner give at this stage an oily, semisolid mass similar in appearance to that obtained from the Elkton silt loam. In only a few cases, however, has sufficient material been obtained to establish its identity as a glyceride.

(To be continued).

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

Ordinary Meeting, January 11th, 1912.

Sir ARCHIBALD GEIKIE, K.C.B., President, In the Chair.

PAPERS were read as follows:—

"*Propagation of Waves through a Stratified Medium, with Special Reference to the Question of Reflection.*" By LORD RAYLEIGH, O.M., F.R.S.

"*Mechanism of the Semipermeable Membrane and a New Method of Determining Osmotic Pressure.*" By Prof. F. T. TROUTON, F.R.S.

The amount of water taken up by a liquid, such as ether, from an aqueous solution, the solute of which is insoluble in the liquid, diminishes as the strength of the solution increases, the maximum amount taken up being from pure water. Reasons are given in the paper for expecting that the amount of water taken up from a given solution would increase under pressure, and further, that at the osmotic pressure of the solution the amount taken up would be the same as that from pure water at the atmospheric pressure.

An account is also given of an experimental investigation which has verified these conclusions in the case of a 60 per cent solution of cane sugar when osmotic pressure is about 80 atmospheres.

"*Mobility of the Positive and Negative Ions in Gases at High Pressures.*" By ALOIS F. KOVARIK, Ph.D.

Rutherford and Child have shown that the current  $i$  per sq. cm., between two parallel plates when an intense



ionisation is confined to the surface of one plate, is given by  $i = g V^2 K / 32 \pi d^3$ , where  $V$  is potential difference,  $d$  distance between plates, and  $K$  mobility of ion. When theoretical conditions are fulfilled, the current through the gas in the two directions affords a direct measure of mobility of positive and negative ions. The surface ionisation was obtained by covering one of the plates with an active preparation of *ionium* separated by Prof. Boltwood from the uranium residues lent by the Royal Society to Prof. Rutherford. Using high pressures, ionisation is mainly confined within a very short distance of the plate. The theory was tested experimentally, and it was found that over a considerable range  $i$  varied as  $V^2$  and inversely as  $d^3$ .

The results for the mobilities of the ions in these gases are as follows:—In dry air and dry hydrogen mobility varies inversely as pressure up to 75 atmospheres, the highest used. In moist carbon dioxide the product of mobility and pressure is constant up to 40 atmospheres, but for higher pressures the product decreases as the gas approaches the liquid state.

The mean values for the products of mobility and pressure in atmospheres, for the range of pressures for which the product was constant, are for negative and positive ions respectively, in dry air 1.89 and 1.346, in dry hydrogen 8.19 and 6.20, and in moist carbon dioxide 0.67 and 0.705 cm. per sec., for a potential gradient of one volt per cm.

"New Method of Determining the Radiation Constant." By G. A. SHAKESPEAR.

The rate of loss of heat of a silvered surface at a temperature of 100° C. in surroundings at 15° C. is observed (a) when the surface is polished, (b) when it is lamp-black. The difference is due to difference in radiation losses. The ratio of the rates of radiation is obtained by exposing the two hot surfaces in turn to a radiomicrometer.

The rate of radiation from the lamp-black is assumed to be proportional to the difference between the fourth powers of the absolute temperatures, 373 and 288. The lamp-black at 100° C. is compared with a full radiator at the same temperature by means of the radiomicrometer. Certain corrections are necessary, and these are dealt with in the paper.

As a check on the comparison given by the radiomicrometer, an instrument which constitutes a closer approximation to a full receiver was devised and used. It was found incidentally that the apparent radiation from lamp-black depends upon the surface upon which the lamp-black is deposited. The value obtained for  $\sigma$  is  $5.67 \times 10^{-8}$  ergs per sq. cm. per sec. per deg.<sup>4</sup>.

"Mechanics of the Water Molecule." By R. A. HOUSTON, M.A., Ph.D., D.Sc.

Suppose that a hydrogen atom loses one electron to a second hydrogen atom, and that the second hydrogen atom loses two electrons to an oxygen atom. Then the oxygen atom has two negative charges, each hydrogen atom one positive charge, there will be one line of force between the first and second hydrogen atoms and two lines of force between the second hydrogen atom and oxygen atom. Let the three lines of force act as equally strong spiral strings, and let a wave of light pass through a medium composed of such molecules. It is shown in the paper, by means of the ordinary theory of dispersion, that the absorption spectrum of such a medium consists of two bands, the ratio of the wave-lengths of which is 2.32. Also from the intensity and width of each band it is possible to calculate  $e/m$  the ratio of unit charge to the mass of the hydrogen atom.

Water is transparent in the ultra-violet and visible spectrum, and has two great bands in the infra red at  $3.07\mu$  and  $6.15\mu$ , which are not present in oxygen or hydrogen. It is shown in the paper that the values of  $e/m$  calculated from these bands are respectively 7110 and 1550 electromagnetic units. Hence the structure assumed for the molecule cannot be far off the truth.

SOCIETY OF CHEMICAL INDUSTRY.  
(LONDON SECTION).

Ordinary Meeting, January 8th, 1912.

Mr. E. GRANT HOOPER in the Chair.

THE following papers were read and discussed:—

"Production of Formic and Acetic Acids by the Atmospheric Oxidation of Turpentine." By C. T. KINGZETT and R. C. WOODCOCK (see p. 26).

"Rapid Volumetric Method for the Estimation of Free Sulphur." By C. DAVIS and J. L. FOUCAR.

The method was devised by Mr. Davis particularly with the view of the rapid estimation of free sulphur in spent oxide, more especially that containing small quantities of organic matter soluble in the usual organic solvents. In the estimation of sulphur in the latter material too high results are obviously given by the extraction test, and an oxidation test is somewhat tedious. The method proposed is to treat the finely powdered and dried material with a solution of sodium cyanide in absolute alcohol, the resulting sulphocyanide being titrated in the usual way.

The results obtained are quite sufficiently accurate for commercial purposes.

"Relative Adsorption of Dyes by Sand and Natural Fibres." By W. P. DREAPER and W. A. DAVIS.

This work deals with the de-solution of dyes passing through a column of sand or textile fibres which have been reduced to an equivalent state by division. Figures are obtained for the relative de-solution effects obtained with solutions in alcohol and water of night blue as the proportion of alcohol increases the amount of dye adsorbed decreases. The relative values for 100 grms. of sand, cotton, and silk being when:—

$y$  = No. of cc. passing colourless through the column, and  $x$  = the per cent of alcohol by volume in the dye solution.  
(Sand)  $y = 120 - 0.315x$ ; (cotton)  $y = 5020 - 110x$ ; and (silk)  $y = 5210 - 110x$ .

The action is a reversible one, and practically all action ceases at a strength of 40 per cent alcohol in each case. The dye precipitated is not the normal night blue, but a very basic hydrochloride, which after extraction in alcohol is insoluble in water.

"Ingrain Dyeing. Influence of certain Groups and Resolution Factor." By W. P. DREAPER.

The effect of the presence of  $\text{NH}_2$  and OH groups in the dye molecule is studied in relation to resolution, or "fastness" of the dye produced against the action of solvents; the reacting units varying in molecular weight from that of  $\beta$ -naphthol to that of primuline itself. Generally speaking, the results agree with those previously obtained by the author with primuline, where the  $\text{NH}_2$  group gives a faster shade against resolution than the corresponding OH one. The influence of  $\text{HSO}_3$  group when present in the first substance applied to the fibre instead of in the so-called developer, or that applied after diazotisation, is that the dye has a much greater resistance against subsequent resolution. Also, that if the two substances, primuline and  $\beta$ -naphthylamine (hydrochloride), are applied respectively to the fibre and after diazotisation coupled with the other one, that in the former case the resistance against resolution may be fifty times as great as in the latter case.

It was noticed by Dreaper and Wilson that if this substance be applied to a low temperature the finally produced dye is not fast against subsequent resolution. It is now observed that if the final dye so produced on the fibre is boiled in water for twenty minutes before resolution, that its resistance under this treatment is greatly increased.

INSTITUTE OF BREWING.  
Ordinary Meeting, January 15th, 1912.

"Fire Protection in a London Brewery." By H. E. FIELD.

The subject is a most interesting one when we consider both the financial loss and the great dislocation to trade which must follow a big fire in a brewery. The system of protection described consists of a powerful stationary pump connected with twenty-six hydrants placed throughout the brewery premises. The pump has a capacity of 550 gallons a minute, the necessary head of steam being kept up day and night (Sundays included). Each hydrant is fitted with several lengths of hose, and by a simple code of signals on an electric bell is in communication with the pump. By these bells an alarm may be given upon which a steam hooter is sounded, and the first jet of water may be relied upon to be at work within one minute of the call, which may be mentioned as being the essential point of any system. The men, specially trained, are drawn from the actual staff, and by regular drills, periodical unexpected calls, and occasional cup competitions are kept up to the mark. Several lantern-slides were shown, one a group of six jets of water; another of one jet over 90 feet high, another a system of cast-iron mains fixed to the walls of some of the buildings with the object of preventing the use of very long lengths of hose. From all the roofs of the outside buildings of the brewery command of neighbours' premises is obtained, and the protection thus afforded to others has, in several instances, proved of immense value to the brewery itself.

Judging by the calls that have been made on their services, and the account the brigade has given of itself during its nineteen years existence, it has fairly shown itself to be no toy, but an organisation of proved utility.

## NOTICES OF BOOKS.

*A Text-book of Inorganic Chemistry.* By GEORGE SENTER, D.Sc. (Lond.), Ph.D. London: Methuen and Co., Ltd. 1911. (6s. 6d.).

THE author of this book shows himself well fitted to write a text-book for the use of students. He knows exactly the weaknesses of the average student, his difficulty in getting a broad outlook, in recognising general principles unless they are pointed out very clearly to him, and in applying them in special cases, and he has a very clear idea of how best to overcome these difficulties. Thus he has produced an eminently practical work which should find extended use in technical schools and colleges. The book is written from an essentially modern standpoint, and the laws of physical chemistry are taken as a basis; special stress is laid upon physical chemistry, and although the descriptive side is by no means neglected, theory is very fully treated, theoretical articles being distributed throughout the book after the facts illustrating them have been put before the student. The whole treatment of the subject is up to date, and the student who makes conscientious use of the book will be thoroughly grounded in inorganic chemistry.

*The London University Guide, 1912.* London: University Correspondence College.

THE London University Guide and University Correspondence Calendar, which is issued gratis, contains the regulations and syllabuses of the University Examinations, with a complete almanac for 1911 and 1912. Short descriptive articles on special subjects are included, and hints on the choice of courses is given for the benefit of intending students of the College, as well as full particulars of all the classes.

*Experimental General Chemistry.* By JAMES H. RANSOM, Ph.D. Second Edition. New York: McGraw-Hill Book Company. 1911.

A VERY brief course in experimental inorganic chemistry is contained in this book. Only the non-metals are treated, and in all about eighty-six experiments are described. Very full questions on the details of each experiment are given, and in addition there are sets of general questions, the answering of which will sometimes involve the study of text-books. To help the student to use his books intelligently and with the minimum waste of time, references are given to several standard works which are almost as well known and as much appreciated in England as in America. Some of these general questions are rather difficult for the students for whom the book is intended, but, on the other hand, they are mostly of a very good type and are such as to stimulate thought and ingenuity. Much attention is paid to the mathematical side of the subject, and there are many problems in calculations.

## CORRESPONDENCE.

### CANADIUM.

To the Editor of the Chemical News.

DEAR SIR,—The notice of the discovery of a new element, "Canadium," which appeared in the CHEMICAL NEWS of December 15, 1911 (vol. civ., p. 283), led me to refer back to the *Transactions of the American Institute of Mining Engineers*, vol. xxxiii., p. 347, in which there appears a notice by William M. Courtis of the discovery of a new element, "Amarillium," in a copper carbonate ore from the Frazer Claims, Similkameen, British Columbia.

The tests to which it answers seem to resemble those of Canadium, and the author gives it as his opinion that the element is a link between the platinum-palladium group and the cobalt-nickel group. It would thus seem to resemble Canadium strongly; possibly they are the same.

No further notice, as far as I can ascertain, has appeared on Amarillium since the publication of the above-mentioned paper in 1903.—I am, &c.,

THOMAS A. EASTICK.

1999 North Ave., Bridgeport, Conn., U.S.A.,  
January 2nd, 1912.

## MEETINGS FOR THE WEEK.

- MONDAY, 22nd.—Royal Society of Arts, 8. (Cantor Lecture). "Ocean Waves, Sea-beaches, and Sandbanks," by Vaughan Cornish, D.Sc.
- TUESDAY, 23rd.—Royal Institution, 3. "The Study of Genetics," by Prof. W. Bateson, F.R.S.
- WEDNESDAY, 24th.—Royal Society of Arts, 8. "A New Process of Hydraulic Separating and Grading," by W. J. Gee.
- THURSDAY, 25th.—Royal Institution, 3. "The New Astronomy," by Prof. A. W. Bickerton.
- Royal Society. "Determination of the Coefficient of Interdiffusion of Gases and the Velocity of Ions under an Electric Force, in Terms of Mean Free Paths," by J. S. Townsend. "The Scattering of  $\alpha$ -Particles," by H. Geiger. "Effect of Temperature upon Radio-active Disintegration," by A. S. Russell. "Relation between Current, Voltage, Pressure, and the Length of the Dark Space in different Gases," by F. W. Aston and H. E. Watson. "Viscosities of Gaseous Chlorine and Bromine," by A. O. Rankine. "Testing of Plane Surfaces," by P. E. Shaw.
- FRIDAY, 26th.—Royal Institution, 9. "The Pressure of a Blow," by Prof. Bertram Hopkinson.
- Physical, 5. Exhibition of a Direct-reading Instrument for Submarine Cable and other Calculations, by R. Appleyard. "The Vibration Galvanometer and its Application to Induction Bridges," by S. Butterworth. "A Negative Result connected with Radio-activity," by J. H. Vincent and A. Bursill. "On Sealing Metals," by P. E. Shaw. "Krypton and the Auroral Spectrum," by T. W. Page.
- SATURDAY, 27th.—Royal Institution, 3. "The Banyoro, a Pastoral People of Uganda—(2) Birth and Death Customs," by The Rev. John Roscoe, M.A.



# THE CHEMICAL NEWS.

VOL. CV., No. 2722.

## THE INTRODUCTION OF PHYSICAL CHEMICAL CONCEPTIONS IN THE EARLY STAGES OF THE TEACHING OF CHEMISTRY.\*

By HARRY C. JONES.

THE question I have been asked to discuss is not a new one, but is, in my opinion, one of fundamental importance. Whenever any great advance has been made in any branch of science the question has arisen, how early should this be incorporated in the teaching of that science; in a word, how closely teaching should follow research? and various answers have been given.

That we are dealing here with a fundamental question is obvious after a moment's reflection. Shall we teach the beginner, in a judicious way, of course, the science as it is at the time in question, or shall we teach him what is not only hopelessly out of date, but what is known to be absolutely untrue?

In answering this question we must take into account that the beginner of to-day is the advanced student of to-morrow, and the chemist of the near future. It is true that most of the beginners in any branch of science never pursue that science at any length, and to these perhaps the least harm is done by teaching the science in an out-of-date manner; but the question becomes more serious when we are dealing with those who propose to devote their lives to the branch of science in question.

Why has the question that we are discussing arisen at this time? As is well known, it has come to the front as the result of certain fundamental discoveries made in chemistry towards the latter part of the last century. These are usually known as *physical-chemical generalisations*, because they were reached through the application of physical methods to chemical problems.

I think the term "physical-chemical" is unfortunate, because it may leave the impression that we are dealing here with something different from chemical, while, in fact, we are not. Indeed, I think the term "physical chemistry" is unfortunate, since it may lead to the conclusions that here is something that is not chemistry, while it is simply an integral part of chemistry. I greatly prefer the term "general chemistry" or "generalised chemistry," since the generalisations which have been reached in this field concern most vitally and fundamentally the whole science of chemistry. This same thought is echoed in the title of Ostwald's great work, "*Lehrbuch der Allgemeinen Chemie*." The term "physical chemistry" is, however, so widely disseminated, and the leading journals in this field in German and French both bear this title, so that the hope of reform in this nomenclature seems remote.

The generalisations that we have in mind are: The discovery of the Law of Mass Action by the Norwegian physicist, Guldberg, and the Norwegian chemist, his son-in-law, Waage, in 1867; the discovery in 1886 of the applicability of the laws of gas pressure to the osmotic pressure of dilute solutions of nonelectrolytes, by one of the greatest men of science who has ever lived, van't Hoff; and the explanation by Arrhenius in the same year of the apparent discrepancies presented by electrolytes, *i.e.*, the announcement of the theory of electrolytic dissociation; of less importance perhaps is the interpretation of chemical valence in terms of Faraday's law, but scarcely so, at least from the pedagogical standpoint; and, finally, the discovery experimentally of the electron by Sir J. J. Thomson, and the instability of the chemical atom by Rutherford.

The question then is, shall these generalisations be taken into account in the early stages of the teaching of chemistry, or shall they not? I know of no productive chemist who doubts the value of introducing them into more advanced stages of work. To do so would be to teach and learn a science of chemistry with the science all left out.

A fair way to judge the value of any discovery is to imagine that it had not been made, and see how the science would be affected by its absence. Similarly, in dealing with a question like the one under discussion, it would seem to me that a logical way to approach it would be to ask: what is lost by not incorporating the modern advances into elementary chemistry, and then what is gained by doing so?

It is certainly true that if we omit these generalisations from the early stages of chemical work we are teaching something that is out of date. There can be no two opinions on this point. But this alone does not solve our problem.

Perhaps the science as developed twenty-five years ago is better adapted to teaching the beginner than is the chemistry of to-day. It is certainly simpler. Why not teach the first year student in chemistry, in addition to a judicious number of the empirical facts of the science, something about the atom and the molecule, and leave it for a later stage to present the more recent developments? What would be lost by so doing? We have now arrived at a fundamental question.

The answer to this question is, in my opinion, that we must no longer teach the chemistry of three or four decades ago, because we know that in many fundamental points it is *untrue*. But it might be answered we grant you this, but for the sake of simplicity we will teach the old chemistry, for, say a year, and then turn the student over to the new.

It is right here that an insuperable difficulty is encountered. It is the *persistence of first impressions*. Anyone who has observed this at all carefully knows how nearly impossible it is to correct erroneous first impressions. Whatever the physiological or psychological explanation of the persistence of these impressions may be the fact remains.

I have had this brought home to me so often and in such a forcible manner that it has made a deep and lasting impression. It has been my lot to try to teach something of the newer developments in chemistry to some students who have been trained in the older school. The result has been that it has required years of incessant drilling to ingraft the new generalisations into the mind of such a student. At first the newer conceptions were scarcely more than tongue deep. In answer to questions it would be stated that at first "it is said that such and such is true," or "the book says," or "you said" that this or that is the explanation, all of which went to show that the new ideas had penetrated hardly more than skin deep, and this, notwithstanding a serious effort on the part of an honest student to make the real science of chemistry an integral part of himself.

What is the explanation of this rather distressing condition of things? *Erroneous first impressions*, from which it is almost impossible to escape.

There is one other matter to which I should like to refer before leaving this part of the discussion. This is the tendency which has existed in the past in this country to make chemistry *easy*. I do not believe there can be much difference of opinion as to this being a fact. How often and how justly have we heard the elementary course in chemistry branded by the student body as a "snap," and for this very reason a preponderating number of students elect this course.

This condition is nothing less than *fatal*, as far as the science of chemistry is concerned, and every serious teacher must study its cause and apply the remedy.

How has this condition come about? Largely, I believe, as follows:—A quarter of a century ago chemistry was

\* Read before the American Chemical Society in Washington, December 27th, 1911.

almost wholly an empirical branch of science. Rowland used to say that chemistry in his day was in the same stage of development as physics in the days of Michael Faraday; and this was only a slightly exaggerated statement. It was necessary at that time to present the subject of chemistry largely by the empirical method. The result was with chemistry, as with any other empirical branch of science, the comprehension of the subject involved primarily, and may I say chiefly, the memory. A reasonably developed memory is much more general than equally well developed reasoning powers, and the use of the latter involves the expenditure of far more mental energy than the use of the former. This is the reason why chemistry was regarded as *easy*. It was something that could be readily memorised.

While this was perhaps a more or less necessary condition several decades ago, those conditions are now largely changed. Chemistry is rapidly advancing along the way to become a branch of exact science, and it can be dealt with to-day in no small measure by the deductive method.

Far be it from my purpose to make chemistry *hard*, or even harder than is necessary for the best good of the science, at least in the early stages of the study of the subject; but a far more important object than to make chemistry *easy* is to make it *scientific*. The object of the teacher should be to make the subject *clear*, but I have not very much respect for making things *easy*, since in science whatever is *easy* is *superficial*. There is no inherent reason why we should make elementary chemistry appreciably easier for the average student than elementary physics; that is to say, make it more superficial.

The argument against introducing the newer generalisations into the elementary teaching of chemistry, based upon the fact that their omission renders the subject easier, is then in reality a strong argument in favour of incorporating them.

The question as to whether it is easier for the teacher to introduce or omit the newer conceptions does not enter into the present discussion, since every efficient teacher is abreast with the development of his science; and, furthermore, in matters of teaching, it is only the best good of the student that is to be considered.

Let us now turn to the other question. What is *gained* by teaching elementary chemistry from the standpoint of the newer generalisations?

A beginner in chemistry soon learns that when a chloride is treated with concentrated sulphuric acid, hydrochloric acid gas escapes, and the chloride is transformed into the corresponding sulphate. At one time this was explained as due to the greater *strength* of sulphuric acid, but we cannot offer this explanation any longer, since we now know that sulphuric acid is only a little more than half as strong as hydrochloric.

The same beginner quickly learns that when a solution of a chloride is treated with a solution of silver nitrate, insoluble silver chloride is precipitated.

These two classes of phenomena are typical of a large number of chemical reactions. In the past such facts were summarised by saying that whenever a gas can be formed it is formed, and whenever a solid can be formed it is formed. This was simply renaming the phenomena in question, but, of course, explained nothing. Yet it was the best that could be done at that time.

It is a very simple matter to give anyone, and therefore a beginner in chemistry, some qualitative conception of the effect of mass or quantity on chemical reactions—chemical reactions being dependent upon two things, the nature of the substances brought together and their relative quantities. If the beginner can grasp one of these conceptions he can grasp the other.

Given the conception of mass and even qualitatively its function in chemistry, the two typical reactions mentioned above can be interpreted, or, indeed, explained.

Hydrochloric acid having a low boiling-point is a gas at ordinary temperatures, and escapes from the field of

action almost as rapidly as it is formed, its active mass being thus reduced nearly to zero.

The silver chloride formed is nearly insoluble in water. It is precipitated as a solid, and its active mass is thus small. I think this treatment renders the two typical reactions more clearly understood, and is more scientific than simply renaming the phenomena.

I venture to predict that not a few students of chemistry, not only of one year's standing but of several, are without any adequate conception of the importance of that condition in which matter in a given state of aggregation is, when mixed with matter in the same or a different state of aggregation—in a word, of the importance of *solution*.

If they were told that the whole science of chemistry is a branch of the science of solutions, they would either not understand the statement at all, or would regard it as a gross exaggeration.

It is a simple matter to make this reasonably clear, at least towards the end of the first year's work in chemistry. By that time enough reactions have been studied to show the student that practically all, if not all, chemical reactions take place in solution, using the term solution in the broad sense in which it is employed to-day. Matter in the pure homogeneous condition is scarcely capable of doing anything chemically, and that the science of solutions is much broader than chemistry will be seen after a moment's reflection. Geology is largely a science of solutions—of aqueous solutions and molten magmas, and how many branches of the biological sciences owe their existence to matter dissolved in other forms of matter?

In the pure homogeneous condition matter is, as we have stated, relatively inert. Nature, and consequently the science of nature is, as it is, primarily due to matter in the dissolved state, and our knowledge of solutions, thanks to van 't Hoff and Arrhenius, is now reasonably satisfactory. We know far more about matter in the gaseous state than in the liquid or solid state. Van 't Hoff has shown us that we can deal with solutions in many fundamental respects as we deal with gases. Consequently we know far more about matter in solution than in the pure homogeneous liquid or solid condition. Why should these facts be concealed from the student of chemistry until late in life?

(To be continued)

## TRANSFORMATION OF OTHER FORMS OF CARBON INTO GRAPHITE.\*

By W. C. ARSEM.

### Introduction.

THE conditions under which "Amorphous Carbon" is transformed into graphite have been the subject of much discussion, and many statements have found their way into the literature which are not supported by experimental evidence. The following theories are commonly held:—

1. A high temperature alone will convert "amorphous carbon" into graphite (Moissan).
2. Pure carbon is not converted to graphite by heat alone (Berthelot).
3. Graphite is the result of intermediate formation and decomposition of carbides, due to the presence of mineral matter as an original constituent, or purposely added (Acheson).

I have collected all available references relating to this problem, and have given briefly the evidence in favour of each theory.

Despretz heated several varieties of carbon in an arc (*Comptes Rendus*, xxix., 709-724). He states that "Any carbon which is submitted for a long time to a high temperature becomes proportionately softer. Finally it is

\* From the *Chemical Engineer*, xiv., No. 4.



transformed into graphite." No physical or chemical tests for graphite are described.

Berthelot (*Ann. Chim. Phys.*, xix., Series 3, 392) was first to recognise the ambiguity in the use of the term "graphite," and proposed the Brodie test as a criterion.

He was not able to convert amorphous carbon to graphite at a white heat in hydrogen. A retort carbon rod which had been ignited, thrust into a stream of oxygen, and quenched in water when fully incandescent, was found to have been graphitised on the tip.

*Work of Moissan* ("Le Four Electrique").—Moissan heated in the arc furnace different varieties of carbon enclosed in carbon crucibles, and, after heating, determined their specific gravity and their behaviour toward nitric acid and potassium chlorate. He found that the products differed in specific gravity, but in all cases they yielded yellow graphitic acid with the oxidising mixture. He concluded that heat alone will convert amorphous carbon into graphite. His results are given in Table I.

TABLE I.

| Carbon.                                                         | Ash after firing.<br>Per cent. | Sp. gr. after firing.<br>Per cent. |
|-----------------------------------------------------------------|--------------------------------|------------------------------------|
| Sugar carbon . . . . .                                          | 0.11                           | 2.19                               |
| Carbon from $Al_2C_3$ . . . . .                                 | —                              | 2.11                               |
| Crystalline graphite from cast-iron, 1150°                      | 1.30                           | 2.17                               |
| Crystalline graphite from cast-iron, high temperature . . . . . | 0.17                           | 2.18                               |
| Crystalline graphite from cast-iron cooled in water . . . . .   | 1.29                           | 2.16                               |
| Graphite from cast-iron by silicon . . . . .                    | 0.85                           | 2.20                               |
| Graphite from platinum . . . . .                                | 1.10                           | 2.06-2.18                          |

He showed also that graphite separates during the cooling of a saturated solution of carbon in various metals, and that graphitic carbon is a product of the decomposition of many carbides, but gives no specific gravity determinations except for Fe and Al.

*Work of Acheson*.—Acheson noted the formation of graphite by the decomposition of silicon carbide at high temperatures. He also noted that the furnace core of bituminous coal coke in the carborundum furnace became converted, to a considerable extent, into graphite. The following statements, made by Acheson, are to be found in the literature and in patents:—

(a). The amount of graphite produced by highly heating pure carbon is insignificant and impracticable, but if the carbon is mixed with considerable mineral matter the yield of graphite is enormously increased (U.S. Patent 568,323, September 29th, 1896).

(b). A mixture of 97 parts coke, or charcoal, and 3 per cent iron oxide, can be changed to a greater or less extent into graphite by varying the time and temperature of heating. As the iron is insufficient to convert all the carbon to carbide it is assumed to have a catalytic effect, first forming a carbide which decomposes, yielding graphite and setting free iron, which again forms carbide, and the cycle is repeated (U.S. Patent 617,979, January 17th, 1899).

(c). A natural variety of carbon containing mineral matter, such as anthracite coal with 5.783 per cent ash, gives practically pure graphite with 0.033 per cent ash. This result is assumed to be due to the intimate admixture of "inherent impurities," it being stated that even with the best artificial mixing and distribution of carbon and mineral matter, the conversion to graphite will be more or less irregular and incomplete (U.S. Patent 645,285, March 13th, 1900).

(d). Petroleum coke, to which has been added 5 per cent iron in the form of oxide, is heated to the vaporising point of iron in a specially constructed electric furnace. The iron vapour is stated to cause conversion of the petroleum coke to graphite (U.S. Patent 711,031, October 14th, 1902).

(e). Acheson also makes the following statements in an

article presented before the Franklin Institute (*Journ. Franklin Inst.*, clxvii., 475, 486).

1. Comparatively pure petroleum coke produces practically no graphite.

2. Impure bituminous coal coke produces large quantities.

3. The larger the known percentage of impurities in the bituminous coal coke the greater the amount produced.

4. Only a part of the core (in the carborundum furnace bituminous coal coke) is converted into graphite, this not being increased even by repeated use of the same grains in successive carborundum furnaces. He concludes: "The amount of graphite produced in the core of the carborundum furnace, and also in graphite articles I have made, is much too great to be accounted for by the theory that it is formed by the dissolution of the fixed carbides formed by the contained impurities, and carbon sufficient to satisfy the chemical formula. The most probable and satisfactory explanation is that a catalytic action occurs a progressive formation and dissolution of carbides. The temperature being much above the point of volatilisation of silica and all other possible impurities, a rapid dissipation of the active agents takes place, and it is completed in this case before the conversion of all the amorphous carbon can occur."

No experimental evidence is given by Acheson to show that pure carbon is not graphitised by simple heating. Direct proof is also lacking to show that a small amount of mineral matter can cause, or facilitate, the conversion of a large amount of carbon to graphite.

The only experiment bearing on this point that I could find described in the literature was in an article by F. A. J. FitzGerald (*Journ. Franklin Inst.*, cliv., 338), from which I quote as follows:—

"Two carbon rods, one composed of very pure lamp black carbon, and containing less than 0.2 per cent ash, the other made of petroleum coke carbon which had been intimately mixed with a certain amount of ferric oxide, were heated side by side in an electric furnace. At the end of the experiment the rod that had contained the iron was found to be graphitic, could be easily cut with a knife, took a beautiful metallic lustre on rubbing, and would mark paper like an ordinary pencil.

"The pure carbon rod showed little change, was dull black in colour, nearly as hard as before heating, and would not leave a mark on paper. One end of this carbon rod, however, was clearly graphite, from the fact that it had been exposed to the action of carbide-forming elements. These vapours had even penetrated to a certain depth in the carbon rod, and in so far as this had occurred the rod showed a brilliant graphitic appearance, was soft, &c."

This experiment would seem to be inconclusive, because two different varieties of carbon were employed, one being heated with iron oxide and the other without. It should have been determined whether or not pure petroleum coke is graphitised when heated without admixture with iron oxide.

Borchers claims that a small amount of Al or  $Al_2O_3$  can convert a considerable quantity of amorphous carbon to graphite ("Elektrometallurgie," 1903, third edition, 564).

He does not state what kind of amorphous carbon is used, or what happens if this carbon be heated without addition of mineral matter, but refers to work by Borchers and Mögenburg ("Graphit aus Amorpher Kohler in Borchers Institut für Metallhüttenwesen und Elektrometallurgie"), which was not available.

Borchers claims priority for the theory that graphite is produced from amorphous carbon by the formation and decomposition of carbides, on the basis of an article in *Zeit. f. Elektrochem.*, March 20th, 1897, iii., 394, from which he quotes: "Metals which form carbides, alloys, or more or less dissociable compounds can assist the crystallisation of carbon." The article mentioned was a discussion of methods for the production of the diamond, no reference being made to graphite in this connection.

Moreover, Moissan (*Ann. Phys. Chem.*, 1896 [7], viii.,

466) had previously prepared graphite by crystallisation of carbon from solution in metals and by decomposition of many carbides.

Other patents relating to the manufacture of graphite are:—

E. G. Acheson, 542,982, July 23rd, 1895. Purifies carbon by volatilising impurities in an electric furnace.

H. Y. Castner, 572,472, December 1st, 1896. Heats rods of retort carbon or other carbon by current. Product has lower density and greater conductivity.

Herbert H. Wing, 598,549, February 8th, 1898. Amorphous carbon converted into graphite by prolonged heating at high temperature. (Ordinary coke mentioned.)

#### Definition of Graphite.

Much confusion has arisen from the uncertainty as to the exact significance of the term "graphite." Many different varieties of graphite have been described, and widely differing values for the various physical constants have been published.

Berthelot was the first to adopt the Brodie test as a criterion (B. C. Brodie, *Liebig's Ann.*, 1860, cxiv., 7). He defined graphite as any variety of carbon which yields graphitic oxide when oxidised with nitric acid and potassium chlorate. Moissan seems to have felt the need of a further criterion, as he defined graphite as a variety of carbon, usually crystalline, having a specific gravity about 2.2, which yields graphitic acid when oxidised.

Some of the uncertainty has been removed by the recent work of Le Chatelier and Wologdine (*Comptes Rendus*, 1908, cxlvi., 49). They showed that a number of natural graphites, when freed from mineral matter and air, had practically the same specific gravity, 2.255, this value being also obtained for a sample of Acheson graphite.

Charpy (*Comptes Rendus*, 1909, cxlviii., 920) considers the density a much better criterion than the Brodie test.

My own work indicates that any variety of carbon, after heating to 3000°, will give a green or yellow oxidation product by the Brodie test, although many samples have a relatively low specific gravity and lack the physical characteristics of graphite. There is no proof that the yellow oxidation product has the same composition in every case. It may be that a variety of structurally related oxidation-products may exist.

It was found, however, on examination of a large number of carbon samples that the graphitic properties become more pronounced as the specific gravity approaches 2.26. We have then either a series of carbons of varying molecular complexity, the end member being graphite, or a series of mixtures of graphite with other forms of carbon. In either case it seems to me that there can be little objection to the following definition:—

Graphite is that allotropic form of carbon having a specific gravity of 2.25 to 2.26.

Those varieties of carbon which have some of the physical properties of graphite, such as colour, softness, and streak, but a lower specific gravity, may perhaps be regarded as impure graphites; that is to say, mixtures of graphite with other forms of carbon.

#### Purpose of the Investigation.

The points at issue are the following:—

1. Can a pure form of carbon be transformed into graphite by simply heating to a high temperature?

2. If this is not the case, is it possible to cause this transformation to occur by heating the carbon, well mixed with a quantity of mineral matter, *insufficient to form carbides* with all the carbon present.

There are two ways of attacking the problem.

(a) To determine the effect of heating various forms of pure carbon alone, and with small amounts of added mineral matter.

(b) To remove the mineral matter from certain varieties of impure carbon, which ordinarily change to graphite when heated, and see if the change will still occur.

Both methods were tried.

(To be continued)

## CHEMICAL NATURE OF SOIL ORGANIC MATTER.\*

By OSWALD SCHREINER and EDMUND C. SHOREY.

(Continued from p. 18).

### ESTERS AND ALCOHOLS (continued).

#### Phytosterol, $C_{26}H_{44}O.H_2O$ .

WHEN the alcoholic extract of the peaty soil, from which lignoceric acid separated on cooling in the manner described in discussing that compound, is carefully evaporated and kept at constant volume by the addition of water until the alcohol is removed there is formed a reddish brown precipitate insoluble in water. This, after separating and drying, forms a red or brown powder of a resinous nature. On extracting this resinous material with boiling petroleum ether there is obtained on removal of the ether a light coloured oily residue, which becomes semisolid on standing. This oily mass was saponified with alcoholic potash, the alcohol removed, and the soap dried and extracted with boiling petroleum ether. The petroleum ether was removed from this extract, and then treated with a relatively large volume of hot alcohol, in which it was completely soluble. On cooling there was a separation of some microcrystalline material (identified as hentriacontane), which was removed by filtration and the alcohol allowed to evaporate. The residue thus obtained was dissolved in a small quantity of chloroform and allowed to stand. After a few hours crystals having the characteristic appearance of phytosterol, the "cholesterol body" of plants, were formed. The form of these crystals, shown in a photomicrograph, is characteristic of this body and is quite distinct from cholesterol itself or from agosterol, another cholesterol body found in soils (*Bull.* 53, Bureau of Soils, U.S. Dept. Agr., 1909; *Journ. Am. Chem. Soc.*, 1909, xxxi., 116).

The compound obtained in this way, when purified by several re-crystallisations melted at 135° C., the melting-point of phytosterol being given by different authorities from 132° C. to 138° C. It gave the Liebermann cholesterol reaction strongly, also the cholesterol reaction with sulphuric acid and chloroform. The method by which the body was obtained, its crystalline form, its melting-point, and colour reactions are sufficient to establish its identity as phytosterol. It should be noted in connection with the isolation of this body that it was obtained as the result of saponification, and it has not been possible to obtain it from the peat soil by any method which did not involve saponification, showing that the phytosterol is present in combination, probably as an ester of a higher fatty acid. Phytosterol is found in nearly all vegetable oils, except olive and palm oils, and is obtained from such sources by saponification, and is, therefore, probably present in such oils, likewise as an ester. The well known wide distribution of phytosterol in plants, and the fact that when found in the soil it is evidently in combination as in plant fats and oils, makes it more than probable that this compound is a plant residue remaining undecomposed in the soil.

In nearly all soils examined there are obtained at some stage of the investigation unsaponified residues which give Liebermann's cholesterol reaction, but, except in the case of agosterol previously described and the phytosterol under discussion, it has not been possible to isolate any definite crystalline cholesterol body. There are a number of bodies of a resinous or unknown nature which give some of the cholesterol reactions. These are particularly abundant in the waxy coating of fruits, and some of them have been described and given names. Vitin  $C_{20}H_{32}O_2$  is one of these compounds (*Monatsh. f. Chem.*, 1893, xiv., 719), but nothing is known of their constitution).

Agosterol, another cholesterol body isolated from soils, has been described in the previous *Bulletin*, and was ob-

\* *Bulletin* No. 74, U.S. Department of Agriculture, Bureau of Soils



tained by a different method than that used for phytosterol, one which did not involve saponification. It is quite evident from the manner in which this compound was isolated that it must occur as such in the soil. The fact that agosterol differs in melting-point and crystalline appearance from any cholesterol body known to exist in natural products, and the fact that it is free and not combined as in natural products, gives some weight to the theory that it may be formed from some other compound such as a fatty acid through the agency of micro-organisms or chemical oxidation.

#### Resin Esters.

In the separation of the so-called resin acids described in a previous section, after shaking the ether solution with the several solutions of alkaline salts, there was left a small quantity of material in the ether. This fraction according to Tschirch contains resin esters.

The material left after evaporation of the ether was a resinous brown powder melting at 95° C., insoluble in water and aqueous alkalis, but readily soluble in alcohol and ether. It contained 0.93 per cent ash, and its elementary composition stated on the ash free basis was found to be:—

|                  | Per cent. |
|------------------|-----------|
| Carbon .. .. .   | 68.88     |
| Hydrogen .. .. . | 10.24     |
| Oxygen .. .. .   | 20.88     |

On saponification with alcoholic potash the resulting soap was not completely soluble in water. The saponification mixture was suspended in hot water, acidified with sulphuric acid, and filtered from the insoluble products formed. The filtrate after cooling was shaken with ether and the ether evaporated. The residue so obtained was in part crystalline, the crystals having the appearance and properties of cinnamic acid. The identity of this crystalline body has, however, not been satisfactorily established and is a small part only of the saponification products.

The other products are for the most part amorphous, and a treatment of the dried mass with petroleum ether separated it into two portions of different appearance and properties, showing that the original material had suffered a change by saponification, and can therefore be considered as an ester.

#### CARBOHYDRATES.

Carbohydrates, represented by sugars, starch, and compound celluloses, make up by far the greater portion of the organic substance of plants and so form the greater part of the material from which soil organic matter is made. The extreme susceptibility of these bodies to fermentation or decomposition by micro-organisms render them probably the most unstable organic material added to soils. Sugars and starch are used by a great variety of bacteria and fungi as food, and no doubt disappear as such long before the cell tissues break up and become part of the soil. The cell wall and fibro-vascular tissues are made up for the most part of a complex compound containing a carbohydrate or cellulose radical. These resist the action of micro-organisms longer, and in the breaking up of the tissues as a result of the decay of the least resistant portions, this complex probably gets into the soil to some extent unchanged.

The products of decomposition of such carbohydrates as starch and sugars are fairly well known, and are for the most part simple compounds, such as alcohol, acetic acid, and carbon dioxide. The more resistant complex, the so-called compound celluloses, contain other groups in addition to the carbohydrate radical, and can give rise in decay to a great variety of products, some of them still quite complex, but resistant to further action of bacteria or fungi. Because of this complexity of the material itself and of its decomposition products, the character of the changes which take place in the decay of this material, either in or out of the soil, are very imperfectly known.

The isolation of carbohydrates from soil is at present confined to a single compound, a pentosan or a body yielding a pentose sugar.

#### Pentosan, $C_5H_8O_4$ .

Nearly all soils when boiled with hydrochloric acid of moderate strength give furfural. The evolution of furfural when an organic mixture is heated with hydrochloric acid is usually regarded as evidence of the presence of pentosans. Pentosans are bodies of a gummy nature and unknown constitution for which the formula  $C_5H_8O_4$  is usually given, that give on heating with acids pentose sugars,  $C_5H_{10}O_5$ , which are definite crystalline bodies of known constitution. These pentose sugars on further heating with acids give furfural, the amount of furfural being proportional to the amount of pentosan or pentose. Based on this fact a method has been devised for determining the pentosan by determining the amount of furfural obtained under certain conditions. This method is adopted as a provisional one by the Association of Official Agricultural Chemists (*Bull.* 107, Revised, Bureau of Chemistry, U.S. Dept. Agr., p. 54).

The method, when applied to soils, generally gives weighable quantities of the phloroglucide, the form in which the furfural is determined. The figures given below show results obtained by this method applied to ten soils of widely different types and character of organic matter. Ten grms. of soil were used, boiled with 12 per cent hydrochloric acid, and the distillation carried on in the usual manner until there was no further evolution of furfural, which was usually the case when the distillate amounted to 300 or 400 cc. The furfural was determined as phloroglucide and the calculation made according to the formula adopted in the provisional method cited.

#### Pentosan in Soils and Relation to Total Carbon.

| Soil.                          | Per cent total carbon. | Per cent pentosan. | Per cent pentosan per 100 of total carbon. | Pentosan carbon per 100 of total carbon. |
|--------------------------------|------------------------|--------------------|--------------------------------------------|------------------------------------------|
| Elkton silt loam .. .          | 0.522                  | 0.176              | 0.079                                      | 15.13                                    |
| Sassafras silt loam .. .       | 0.315                  | 0.055              | 0.025                                      | 7.93                                     |
| Chester silt loam .. .         | 1.510                  | 0.182              | 0.083                                      | 5.49                                     |
| North Carolina peaty soil .. . | 27.102                 | 1.090              | 0.495                                      | 1.83                                     |
| Marshall loam .. .             | 6.971                  | 2.750              | 1.249                                      | 17.93                                    |
| California peaty soil .. .     | 11.478                 | 0.341              | 0.150                                      | 1.30                                     |
| Norfolk fine sandy loam .. .   | 0.822                  | 0.027              | 0.012                                      | 1.46                                     |
| Santa Paula, Cal., loam .. .   | 1.308                  | 0.061              | 0.028                                      | 2.14                                     |
| Portsmouth loam .. .           | 3.854                  | 0.219              | 0.099                                      | 2.57                                     |
| Susquehanna clay loam .. .     | 1.048                  | 0.659              | 0.299                                      | 28.53                                    |

The figures given here illustrate well, perhaps better than any others available, the great variation of organic matter in soils. In these ten soils selected somewhat at random the pentosan carbon per 100 of total carbon varies from 1.30 to 28.53, while the third lowest result, 1.83, was obtained from a soil containing the largest quantity of organic matter.

The Marshall loam, containing the largest quantity of pentosan, 2.75 per cent, was selected for further investigation. An alkaline extract of this soil was made by treating it for several hours with 2 per cent sodium hydrate, the dark coloured extract syphoned off, and the humus bodies precipitated by acidifying with acetic acid, the filtrate made neutral, and filtered from the precipitate formed. Lead acetate in excess was added to the neutral filtrate, resulting in the formation of a heavy brown precipitate and the removal of nearly all the colour from the solution. To the filtrate from this precipitate dilute ammonia was carefully added, when a light yellow voluminous precipitate was formed. This, after washing, was suspended in water and treated with dilute sulphuric acid, avoiding excess. The lead sulphate was removed by filtration and the filtrate concentrated to a small volume. To this solution three volumes of 95 per cent alcohol were added, when a gummy precipitate was formed, which, after washing

with alcohol, dried to a hard translucent mass. This mass contained traces of lead, which it retained very persistently. It was soluble in alkalis, and formed an opalescent mucilage with water. On heating with 12 per cent hydrochloric acid furfural was given off freely, and on heating with phloroglucin and hydrochloric acid the characteristic purple colour reaction for pentose sugars was obtained. On digesting for some time with sulphuric acid of moderate strength and neutralising, a solution was obtained which reduced Fehling's solution and gave an osazone melting at 160° to 161° C. On treating with cadmium carbonate and bromine according to the method of Bertrand (*Bull. Soc. Chim.*, 1891, [3], v., 556), the characteristic crystals of the double salt cadmium xylonate and cadmium bromide were obtained, showing the presence of xylose as one of the products of hydrolysis of the substance isolated from the soil. Tests made for the presence of other pentose sugars gave negative results.

The quantitative method of determining pentosans depends, as has been noted, on the formation of a pentose from the pentosan and the formation of furfural from the sugar on further heating with acid. In the cell wall material, which makes up such a large portion of the organic matter of plants, there is no doubt a pentosan body present, either as such or as part of the complicated molecule of lignocellulose, for a crude pentosan can be prepared from such material. In the case of the Marshall loam such a crude pentosan was obtained, and was probably present as such in the soil as a plant residue. In the case of soil organic matter in general, however, it can not be assumed that the formation of a pentose sugar, and from it furfural, necessarily indicates the presence of a pentosan as such. Pentose sugars are part of the complicated molecules of nucleo-proteids and phosphatids, and are split off from these on heating with acids. The nucleo-proteids are characteristic of tissues in which nucleated cells are abundant and those of animal origin have been especially studied. The investigation of those of plant origin is not so thorough, but there is every evidence that the parts of plants rich in cells are also rich in nucleo-proteids and this compound and its decomposition products must contribute to the organic matter of the soil.

With this in mind it is evident that a determination of pentosan in soil by the method in general use is simply the determination of the furfural that may arise from a pentosan, a pentose, or a pentose yielding material other than a pentosan.

In the light of our present knowledge of pentosans and pentose-yielding material, their presence in a soil must be regarded either as a plant residue which has resisted decomposition, such as a portion of the lignocellulose, or as products of decomposition of complicated bodies, such as nucleo-proteids.

#### NITROGENOUS COMPOUNDS.

In the previous sections organic compounds containing carbon, hydrogen, and oxygen only have been discussed. All living matter has as essential components some organic compounds that contain nitrogen in addition to carbon, hydrogen, and oxygen. In consequence, soils also contain compounds of the same character or those arising from them through decomposition. In organic life the nitrogenous compounds are for the most part those related to protein, either those from which protein is built up or those resulting from its decomposition. In these some of the nitrogen is always linked with hydrogen in the amino form,  $\text{NH}_2$ , some of it in more complex compounds being in the imino,  $\text{NH}$ , form. In consequence of this structure, protein itself and its nitrogenous decomposition products are either basic or are what may be called potential bases.

In the decomposition of protein there are two groups of nitrogenous compounds, the monamino, and the diamino acids, also called hexone bases. Both contain the carboxyl group  $\text{COOH}$ , and in the monamino acids there is but one  $\text{NH}_2$  group and the compounds are

mainly acid in character. Many of them, however, have the property of forming compounds with both acids and bases. Glycocoll,  $\text{CH}_2\text{NH}_2\text{COOH}$ , leucine,  $\text{CH}_2(\text{CH}_2)_3\text{CHNH}_2\text{COOH}$ , and glutamic acid,  $\text{COOH}(\text{CH}_2)_2\text{CHNH}_2\text{COOH}$ , are examples of this mon-amino acid group.

In the diamino acids or hexone bases there are two or more  $\text{NH}_2$  groups and sometimes an  $\text{NH}$  group and the basic character usually predominates; lysine,  $\text{CH}_2\text{NH}_2(\text{CH}_2)_3\text{CHNH}_2\text{COOH}$ , and diamino propionic acid,  $\text{CH}_2\text{NH}_2\text{CHNH}_2\text{COOH}$ , are examples of this group.

In addition to protein, which breaks up into amino acids, there are in the cell nucleus what are known as nucleo-proteids, already referred to in discussing pentose yielding material. These nucleo-proteids are combinations of protein with a nonprotein radical. This non-protein radical, known as nucleic acid, is a complex body of unknown constitution, but its decomposition products are well known. These are:—Phosphoric acid, a characteristic and constant product; pentose sugar, usually present; lævulinic acid, sometimes present; pyrimidine derivatives, always present; and purine bases, always present. These last two groups are nitrogenous compounds, and differ in several respects from the amino acids. They contain no carboxyl, they are of ring formation, and the nitrogen may be either uncombined or combined with hydrogen, as  $\text{NH}$  or as  $\text{NH}_2$ .

The pyrimidine derivatives known as decomposition products of nucleic acid are uracil,  $\text{C}_4\text{H}_4\text{N}_2\text{O}_2$ , cytosine,  $\text{C}_4\text{H}_5\text{N}_3\text{O}$ , and thymine,  $\text{C}_5\text{H}_6\text{N}_2\text{O}_2$ . The other group, the purine bases, are derivatives of a body purine which in its turn is closely related to pyrimidine. The chief members of this group are xanthine,  $\text{C}_5\text{H}_4\text{N}_4\text{O}_2$ , hypoxanthine,  $\text{C}_5\text{H}_4\text{N}_4\text{O}$ , adenine,  $\text{C}_5\text{H}_5\text{N}_5$ , and guanine,  $\text{C}_5\text{H}_5\text{N}_5\text{O}$ .

Among the nitrogenous compounds isolated from soils there are representatives of three of the above-mentioned groups resulting from the decomposition of protein or nucleo-proteids, viz., diamino acids, pyrimidine derivatives, and purine bases.

To the nitrogenous groups here mentioned as having been found in soils, must be added the pyridine group represented by the picoline carboxylic acid, the presence of which in soils was reported upon in the earlier work cited.

(To be continued).

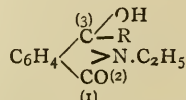
## ISOMERIC PHENYLPHthalIMIDES AND SOME ALLIED COMPOUNDS.\*

### II.

By MITSURU KUHARA and SHIGERU KOMATSU.

(Continued from p. 31).

It has already been shown by Sachs and Ludwig (*Ber.*, xxxvii., 385) that when magnesium alkyl haloids react with ethylphthalimide, alkyloxy-derivatives of isoindolinone (phthalimidine) are produced, as will be seen:—



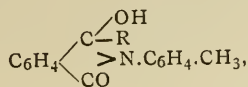
2-Ethyl-3-alkyl-3-oxy-isoindolinone.

Following their statements, the authors studied at first the action of magnesium alkyl haloids upon two isomeric orthotolylphthalimides, and found that, in fact, there is formed one and same product from both compounds, which

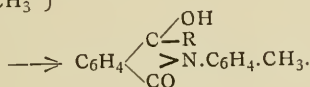
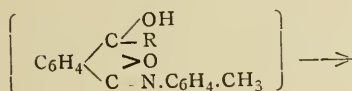
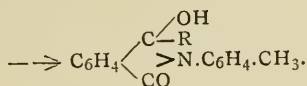
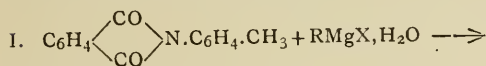
\* *Memoirs of the College of Science and Engineering, Kyoto Imperial University*, ii., No. 12.



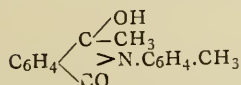
is assumed to be 2-orthotolyl-3-alkyl-3-oxy-isindolinone (according to Sachs and Ludwig's nomenclature),—



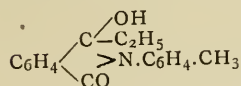
inferring its production from the analogy with that of the indolinone derivative above referred to. Then, the authors have brought forward the explanation for the formation of the identical substance from two isomeric orthotolyl-phthalimides upon the assumption that 2-orthotolyl-3-alkyl-3-oxy-isindolinone may be produced directly from the normal orthotolylphthalimide, but indirectly from asymmetrical orthotolylphthalimide by the molecular rearrangement of an intermediate product, as may be represented by the following schemes of reaction :—



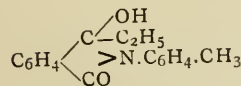
On continuing the same process of the Grignard reaction with *s*- and *a*-paratolylphthalimides, *s*- and *a*-*as*-metaxylylphthalimides, and *s*- and *a*-pseudocumylphthalimides, the corresponding derivatives of isindolinone were found to be formed. All the compounds thus obtained by the authors are recorded in the following table :—



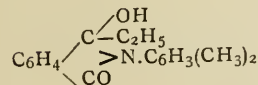
2-orthotolyl-3-methyl-3-oxy-isindolinone.



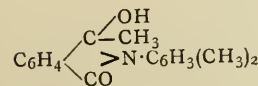
2-orthotolyl-3-ethyl-3-oxy-isindolinone.



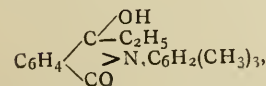
2-paratolyl-3-ethyl-3-oxy-isindolinone.



2-*as*-metaxylyl-3-ethyl-3-oxy-isindolinone.



2-*as*-metaxylyl-3-methyl-3-oxy-isindolinone.



2-pseudocumyl-3-ethyl-3-oxy-isindolinone.

# EXPERIMENTAL PART.

## 1. *a*-Orthotolylphthalimide, $\text{C}_6\text{H}_4 \begin{cases} \text{C} = \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3 \\ \text{CO} \end{cases} > \text{O}$

An ethereal solution of phthalyl chloride (1 mol.) was carefully added drop by drop to an ethereal solution of orthotoluidine (3 mols.), each solution having been previously cooled to  $-10^\circ$  in a freezing mixture of ice and salt. The reaction immediately took place, giving a yellow precipitate after each addition. The whole mixture was allowed to stand for a while in the freezing mixture, and the precipitate, then separated from the mother-liquor by filtration, was washed successively with ice-cold hydrochloric acid, ammonia, and cold water. The residue was observed to consist of a mixture of two different compounds, yellow and colourless, which were separated by treating with ether. The compound which is difficultly soluble in ether, and crystallises from hot alcoholic solution in colourless needles, was found to possess all the properties of normal orthotolylphthalimide (*Ber.*, xvii., 2679; *Ann. d. Chem.*, ccxxvii., 206; *Am. Chem. Journ.*, ix., 52), while the substance soluble in ether crystallises in canary-yellow needles, and melts at  $136-137^\circ$ . The latter is readily soluble in ether, alcohol, benzene, and chloroform. It changes to normal orthotolylphthalimide on heating with hydrochloric acid, or with alkali, possibly by the molecular rearrangement.

The substance dried over sulphuric acid gave on analysis the following results :—

- I. 0.222 grm. of the substance gave 0.6238 grm.  $\text{CO}_2$  and 0.102 grm.  $\text{H}_2\text{O}$ .
- II. 0.449 grm. of the substance gave 0.0239 grm. N.
- III. 0.5034 grm. of the substance gave 0.0291 grm. N.
- IV. 0.5012 grm. of the substance gave 25.2 cc. N. ( $25^\circ$ , 758 mm.).

|             | Calculated for<br>$\text{C}_6\text{H}_4 \begin{cases} \text{C} = \text{N} \cdot \text{C}_6\text{H}_4 \cdot \text{CH}_3 \\ \text{CO} \end{cases} > \text{O}$ | Found. |      |      |      |
|-------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------|--------|------|------|------|
|             |                                                                                                                                                             | I.     | II.  | III. | IV.  |
| Carbon ..   | 75.95                                                                                                                                                       | 76.17  | —    | —    | —    |
| Hydrogen .. | 4.64                                                                                                                                                        | 5.09   | —    | —    | —    |
| Oxygen ..   | 13.50                                                                                                                                                       | —      | —    | —    | —    |
| Nitrogen .. | 5.91                                                                                                                                                        | —      | 5.33 | 5.78 | 5.57 |

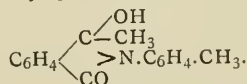
The determination of its molecular weight by the ebullioscopic method, using chloroform as a solvent, gave the following results :—

Molecular elevation for chloroform =  $35.9$ .

| Expt.               | Solvent (grms). | Substance (grm.).                                          | $\Delta$ .     | Mol. wt. |
|---------------------|-----------------|------------------------------------------------------------|----------------|----------|
| 1.                  | 34.50           | 0.1254                                                     | 0.068°         | 192      |
| 2.                  | 34.50           | 0.2397                                                     | 0.120          | 208      |
| 3.                  | 34.50           | 0.3302                                                     | 0.175          | 196      |
| 4.                  | 34.50           | 0.4057                                                     | 0.225          | 188      |
|                     |                 | Calc. for $\text{C}_{15}\text{H}_{11}\text{O}_2\text{N}$ . | Found as mean. |          |
| Molecular weight .. |                 | 237                                                        | 196            |          |

The substance is evidently different from *a*-orthotolylphthalimide previously obtained by one of us and Fukui, and the constitution of the latter or even its existence has now become uncertain, as the substance under consideration, which must possess a decidedly unsymmetrical constitution, has been discovered by us.

## 2. 2-Orthotolyl-3-methyl-3-oxy-isindolinone,—



Two grms. magnesium, 16 grms. methyl iodide, and 30 grms. anhydrous ether, mixed with a trace of iodine, were placed in a round-bottomed flask provided with a reflux condenser; after a while violent reaction took place with the gradual dissolution of magnesium. To the

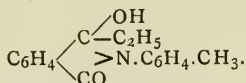
Grignard reagent so prepared 10 grms. of *s*- or *a*-orthotolylphthalimide were added in small portions. After twenty hours, the ether was removed by distillation, and the product was decomposed by adding ice and dilute sulphuric acid. The product of decomposition was extracted with ether, and the solution acquired a violet colour owing to the presence of a violet coloured compound whose chemical nature has not been ascertained yet.

On allowing the ethereal solution to evaporate, after treating with animal charcoal, colourless platy crystals were formed. The substance is soluble in ether, alcohol, and chloroform, and melts at 161–162°. It gave, on analysis, the following results:—

- I. 0.259 grm. of the substance gave 0.7251 grm. CO<sub>2</sub> and 0.144 grm. H<sub>2</sub>O.  
II. 0.5077 grm. of the substance gave 26.2 cc. N (22°, 753 mm.).

| Calculated for                                                                                  |       | Found. |      |
|-------------------------------------------------------------------------------------------------|-------|--------|------|
| $C_6H_4 \begin{cases} C \begin{cases} >C_3H_5 \\ >N.C_6H_4.CH_3. \end{cases} \\ CO \end{cases}$ |       | I.     | II.  |
| Carbon .. ..                                                                                    | 75.89 | 76.42  | —    |
| Hydrogen .. ..                                                                                  | 5.93  | 76.21  | —    |
| Oxygen .. ..                                                                                    | 12.65 | —      | —    |
| Nitrogen .. ..                                                                                  | 5.53  | —      | 5.78 |

3. 2-Orthotolyl-3-ethyl-3-oxy-isindolinone,—



Magnesium ethyl iodide and *s*- or *a*-orthotolylphthalimide were mixed together in the molecular proportion of 3 to 1, and the product was treated as in the preceding case.

The substance crystallises in colourless plates from alcohol, and melts at 169–171°. It is soluble in ether and alcohol. Its analysis is as follows:—

- I. 0.209 grm. of the substance gave 0.585 grm. CO<sub>2</sub> and 0.1332 grm. H<sub>2</sub>O.  
II. 0.3584 grm. of the substance gave 15.8 cc. N (24°, 755 mm.).  
III. 0.3535 grm. of the substance gave 17.9 cc. N (25°, 760 mm.).

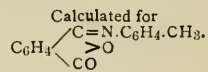
| Calculated for                                                                                  |       | Found. |      |      |
|-------------------------------------------------------------------------------------------------|-------|--------|------|------|
| $C_6H_4 \begin{cases} C \begin{cases} >C_3H_5 \\ >N.C_6H_4.CH_3. \end{cases} \\ CO \end{cases}$ |       | I.     | II.  | III. |
| Carbon .. ..                                                                                    | 76.41 | 76.44  | —    | —    |
| Hydrogen .. ..                                                                                  | 6.37  | 7.08   | —    | —    |
| Oxygen .. ..                                                                                    | 11.98 | —      | —    | —    |
| Nitrogen .. ..                                                                                  | 5.24  | —      | 4.90 | 5.66 |

4. *a*-Paratolylphthalimide,  $C_6H_4 \begin{cases} C \begin{cases} >C_3H_5 \\ >N.C_6H_4.CH_3. \end{cases} \\ CO \end{cases}$

This substance was formed simultaneously with normal or *s*-paratolylphthalimide (*Ber.*, x., 2679; xvi., 1320; xvii., 2679) from paratoluidine and phthalyl chloride under the conditions similar to those observed in the formation of *a*-orthotolylphthalimide.

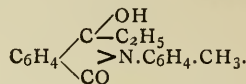
It is soluble in ether, alcohol, benzene, acetone, and chloroform, and crystallises in light yellow needles. It melts at 109–110°. The substance dried over sulphuric acid was analysed:—

- I. 0.2062 grm. of the substance gave 0.1018 grm. H<sub>2</sub>O and 0.5702 grm. CO<sub>2</sub>.  
I. 0.2092 grm. of the substance gave 10.1 cc. N (15°, 765.7 mm.).



| Calculated for                                                                                  |       | Found. |      |
|-------------------------------------------------------------------------------------------------|-------|--------|------|
| $C_6H_4 \begin{cases} C \begin{cases} >C_3H_5 \\ >N.C_6H_4.CH_3. \end{cases} \\ CO \end{cases}$ |       | I.     | II.  |
| Carbon .. ..                                                                                    | 75.95 | 75.41  | —    |
| Hydrogen .. ..                                                                                  | 4.64  | 4.91   | —    |
| Oxygen .. ..                                                                                    | 13.50 | —      | —    |
| Nitrogen .. ..                                                                                  | 5.91  | —      | 5.69 |

5. 2-Paratolyl-3-ethyl-3-oxy-isindolinone,—



By decomposing the reaction product of magnesium ethyl iodide and *s*- or *a*-paratolylphthalimide by means of ice and dilute sulphuric acid, a brown coloured substance was obtained. From its ethereal solution, colourless needle shaped crystals separated out. The substance is soluble in ether and alcohol, and melts at 177–178°. It was analysed, and the results are as follows:—

- I. 0.1616 grm. of the substance gave 0.45 grm. CO<sub>2</sub> and 0.097 grm. H<sub>2</sub>O  
II. 0.1734 grm. of the substance gave 8.2 cc. N (13°, 758.8 mm.).

| Calculated for                                                                                  |       | Found. |      |
|-------------------------------------------------------------------------------------------------|-------|--------|------|
| $C_6H_4 \begin{cases} C \begin{cases} >C_2H_5 \\ >N.C_6H_4.CH_3. \end{cases} \\ CO \end{cases}$ |       | I.     | II.  |
| Carbon .. ..                                                                                    | 76.41 | 76.17  | —    |
| Hydrogen .. ..                                                                                  | 6.37  | 6.69   | —    |
| Oxygen .. ..                                                                                    | 11.98 | —      | —    |
| Nitrogen .. ..                                                                                  | 5.24  | —      | 5.57 |

(To be continued).

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

Ordinary Meeting, January 18th, 1912.

Sir ARCHIBALD GEIKIE, K.C.B., President, followed by Sir A. B. KEMPE, Vice-President, in the Chair.

PAPERS were read as follows:—

"Physiological Effects of Low Atmospheric Pressures, as Observed on Pike's Peak, Colorado." By J. S. HALDANE, M.D., LL.D., F.R.S.; C. GORDON DOUGLAS, B.M.; YANDELL HENDERSON, Ph.D., Yale University Medical School; and EDWARD C. SCHNEIDER, Ph.D., Colorado College.

The following is a short preliminary account of a series of observations made in the summer of 1911 on the summit of Pike's Peak, Colorado.

Pike's Peak is 14,107 feet above sea-level, the barometric pressure on the summit being about 18 inches (457 mm.). There is an excellent stone house close to the summit, in which we were accommodated during our stay of five weeks. The main object of the expedition was to discover to what extent, and by what means, adaptation takes place to low barometric pressure and consequent deficiency in the partial pressure of oxygen in the air.

Our chief conclusions are as follows:—

1. After two or three days on the summit of Pike's Peak very distinct signs of acclimatisation began to appear.
2. Before acclimatisation occurred, blueness of the lips and face, nausea, intestinal disturbance, headache, fainting in some persons, and periodic breathing were observed, besides great hyperpnœa on exertion or holding the breath for a few seconds.
3. All these symptoms are referable, directly or indirectly, to want of oxygen produced by the diminished



partial pressure of oxygen in the air. We did not observe, either in ourselves or in the large number of persons who ascended the Peak, any symptoms (apart from the effects of the bright light) not referable to the same cause.

4. After acclimatisation had occurred these symptoms disappeared, with the exception that hyperpnoea on exertion or on holding the breath for a few seconds was still much greater than usual. Periodic breathing was still observed occasionally, and blueness of the lips and face was present after continuous and powerful exertion, such as walking up hill.

5. The respiratory exchange during rest remained about normal in the one subject on whom exact experiments were made, and the respiratory exchange during work did not appear to be markedly increased.

6. After acclimatisation the alveolar carbon dioxide pressure was diminished from about 40 mm. to about 27 mm. during rest or moderate exertion, which corresponded to an increase of about 50 per cent in the ventilation of the lung alveoli. During severe exertion the alveolar carbon dioxide pressure was about half what it normally is during similar exertion, which corresponded to an increase of about 100 per cent in the hyperpnoea; and owing to a temporary alteration in the respiratory quotient the breathing was still further increased, so that it was for a time increased to thrice what it would have been at sea-level with the same oxygen consumption.

7. The change in the level of alveolar carbon dioxide pressure occurred gradually after going up, and disappeared gradually on coming down, the change taking a number of days to reach completion.

8. The percentage of hæmoglobin in the blood increased for several weeks on the summit of Pike's Peak, and varied in different acclimatised persons from 115 to 154 per cent on the scale of the Gowers-Haldane hæmoglobinometer, corresponding to an oxygen capacity of from 21 to 28.5 cc. of oxygen per 100 cc. of blood. The number of red corpuscles per cubic mm. of blood increased parallel with the hæmoglobin, and the percentage volume of red corpuscles, as determined by the hæmatocrit, also increased in proportion to the percentage of hæmoglobin.

9. A large increase in the total amount of hæmoglobin (determined by the carbon monoxide method) in the body occurred during the first three weeks, and along with this increase there was found, except in the first week, a slight increase in blood volume, as well as the increase, already referred to, in the percentage of hæmoglobin.

10. On coming down from Pike's Peak the hæmoglobin percentage diminished much more rapidly than the total hæmoglobin, so that the blood volume was still further increased at first. It required about four weeks for the excess of hæmoglobin and blood volume to disappear, though the hæmoglobin percentage fell to normal much earlier.

11. So far as we could ascertain there was very little change in the rate of circulation on Pike's Peak after acclimatisation. Pulse and blood pressure were but little affected. In most cases, however, there was a slight increase in the pulse rate.

12. After acclimatisation the oxygen pressure in the arterial blood (measured by the carbon monoxide method) rose during rest to about 35 mm. of mercury, or 66 per cent above the alveolar oxygen pressure, and remained at a level of only about 12 mm. below the normal oxygen pressure at sea-level. Immediately after ascending the Peak, and before acclimatisation had occurred, the arterial oxygen pressure was found to be about 45 mm. below normal, and only slightly above the alveolar oxygen pressure. This change appears to be due to a progressive increase in the activity of the alveolar epithelium in secreting oxygen inwards. On raising the alveolar oxygen pressure to normal, the difference between alveolar and arterial oxygen pressure diminished rapidly.

13. Acclimatisation to high altitudes is due mainly to the increased secretory activity of the alveolar epithelium, but partly also to the increased lung ventilation, and to a

lesser extent to the increased hæmoglobin percentage in the blood. The acclimatisation takes some days to develop. During rapid ascents in balloons or aeroplanes it would not have time to develop, and this explains the contrast between the experience of balloonists, &c., and that of mountaineers who ascend gradually.

"Effect of Altitude upon the Dissociation Curve of the Blood." By J. BARCROFT, F.R.S.

The affinity of hæmoglobin for oxygen depends, among other things, upon the hydrogen ion concentration of the blood. After removing the CO<sub>2</sub> from blood, a scale was made out for the blood of each person plotting the percentage of oxyhæmoglobin at a standard oxygen pressure vertically, and the amount of acid added to the blood horizontally. Thus by estimating the percentage of oxygen in the hæmoglobin of blood at high altitudes an estimate can be made of the acid which has been contributed to it by the organism. It thus appeared that at each altitude the alkalinity of the blood decreased (apart from CO<sub>2</sub>). This was so in the resting individual, but much more markedly so during exercise.

The dissociation curve of blood exposed to the CO<sub>2</sub> pressure of the alveolar air confirmed the result that during rest the dissociation curve remains constant. During activity the affinity of the blood for oxygen decreases, and the hæmoglobin is able to unite with less oxygen in the lung, and to do so at a lower rate. On the other hand, the rate of dissociation in the tissues increases. The acid which accumulates in the blood is not lactic acid entirely, and during rest only to a slight extent. The persons whose blood was most alkaline (apart from CO<sub>2</sub>) were most prone to sickness.

"Note on *Astrosclella willeyana*, Lister." By R. KIRKPATRICK.

"*Herpetomonas pediculi*, nov. spec., Parasitic in the Alimentary Tract of *Pediculus vestimentis*, the Human Body-Louse." By H. B. FANTHAM, D.Sc., B.A.

"An *Antelope Trypanosome*." By CAPT. A. D. FRASER, R.A.M.C., and DR. H. L. DUKE.

## AMERICAN CHEMICAL SOCIETY.

### WASHINGTON MEETING.

AGAIN the American Chemical Society has held the largest meeting in its history, 658 members and guests registering in Washington, and probably 700 were present.

The meeting opened on Wednesday, December 27th, with a joint meeting of the Section on Chemical Education and the Division of Physical and Inorganic Chemistry, at which the following four papers were given:—

"The Teaching of Physical Chemistry." By A. A. Noyes, Chairman.

"Physical Chemistry in the Introductory Course." By W. D. Bancroft.

"The Introduction of Physical Chemical Conceptions in the Early Stages of the Teaching of General Chemistry." By H. C. Jones. (See p. 37).

"Some Applications of Colour Photography in the Teaching of Physical Chemistry." (Illustrated.) By J. Howard Mathews.

In the afternoon the address of Vice-President Frankforter, of Section C, entitled "The Resins and their Chemical Relations to the Terpenes," was delivered before a large audience, and was followed by an address by Chairman H. P. Talbot, on the subject "Privileges and Responsibilities of the Chemical Analyst." Following Dr. Talbot, Dr. A. L. Voge, of the Library of Congress, read a paper on "Ostwald's Proposed International Institute of Chemistry."

Throughout the week the Society's Divisions of Agricultural and Food Chemistry, Biological Chemistry, Industrial Chemists and Chemical Engineers, Fertiliser Chemistry, Organic Chemistry, Pharmaceutical Chemistry, Physical and Inorganic Chemistry, and the Chemistry of

Indiarubber held meetings in rooms especially assigned to them.

Some 500 were present at the "smoker" on Wednesday evening, which was fully up to the standard of the well-known smokers of the Chemical Society.

On Thursday evening Alexander Smith, President of the Society, delivered his presidential address, entitled "An Early Physical Chemist," and was followed by an interesting lecture by Frank B. Kenrick and H. E. Howe, consisting chiefly of illustrations by means of the lantern of the effect of temperature, pressure, concentration, surface tension, osmotic pressure, &c., on reactions in heterogeneous systems.

A feature of the divisional meetings was the Symposium on Mineral Wastes and their Conservation, held before the Division of Industrial Chemists and Chemical Engineers on Friday. The following papers were presented, and the discussion was prolonged throughout the day:—

"Carbon Waste." By J. A. Holmes.

"Zinc Losses in Brass Manufacture" and "Need of Special Alloys for Special Uses." By W. H. Bassett.

"New Uses to Reduce Abuses in Conservation." By W. R. Whitney.

"Wastes in the Ceramic Industry." By A. V. Bleininger.

"The Abuse of Brand." By A. D. Little.

"Waste and Conservation of Potash and Phosphoric Acid." By F. K. Cameron.

"Sulphur Fumes and Flue Dust." By F. G. Cottrell.

"Miscellaneous Mineral Wastes." By Charles L. Parsons.

This programme, together with the papers given, will be featured in the March *Journal of Industrial and Engineering Chemistry*.

The Division of Pharmaceutical Chemistry held a Symposium on Drug Assaying on Friday morning, and on Friday afternoon a joint meeting of the Society of Biological Chemists was held with the biological chemists of the American Chemical Society.

The Secretary's report showed an increase of members of over 500 for the year, the Society's membership standing on December 1st at 5603. During the year the Society spent over 55,000 dols. on its journals, returning to each paid member in actual cost of publications more than 100 per cent of his dues.

At the meeting of the Council on Tuesday afternoon and evening, the Biological Section of the Society was authorised to form a Biochemical Division, electing its own officers, and two new Local Sections were formed, one at Detroit and one at New Haven.

Interesting reports were received from the Committee on Standard Methods of Analysis, and from the Committee on Patent and Related Legislation.

It was voted to donate the library of the American Chemical Society to the New York Chemists' Club, on condition that members of the Society have ready access thereto.

The question of the time of the annual meetings of the Society was vigorously discussed, many members favouring a change from the winter season to Easter week, and a committee was appointed to take this into consideration and report to the Council.

The election of the following officers was announced for 1912:—A. D. Little, President; C. L. Parsons, Secretary; A. P. Hall, Treasurer; W. A. Noyes, Editor of the *Journal of the American Chemical Society*; A. M. Patterson, Editor of *Chemical Abstracts*; M. C. Whitaker, Editor of the *Journal of Industrial and Engineering Chemistry*; E. G. Love and Alexander Smith, Directors for two years; S. W. Parr, W. H. Walker, W. L. Miller, and W. D. Bigelow, Councillors at Large for three years; C. H. Herty, Councillor at Large to fill the unexpired term of A. D. Little; E. G. Love, G. C. Stone, and A. E. Hill, Finance Committee; Wm. McMurtrie, C. L. Parsons, and B. E. Curry, Membership Committee.

Over 250 papers were presented at the meeting, abstracts of many of which will appear shortly in *Science*.

## NOTICES OF BOOKS.

*Elementary Experimental Chemistry.* By F. E. WESTON, B.Sc. (Lond.), F.C.S. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1911.

This book contains a course of experimental chemistry suitable for young students beginning the subject, and appears to fulfil its aim of laying a sound foundation for subsequent more detailed and difficult work. Experiments on solution, air, water, the commoner chemical substances, &c., are very fully described; they are well graduated in difficulty and are excellently illustrated by photographs of apparatus. No symbols or formulæ are employed. Some quantitative work is introduced in the later parts of the book, including the verification of the fundamental laws and the determination of equivalent weights. Frequent allusions are made to the classical literature of chemistry, and the treatment is such as to give the student some knowledge of the history of the development of the science. The directions are very clear, and should allow no possibility of failure or of unsatisfactory results if they are carefully followed. In some cases it seems unnecessary, and in fact inadvisable, that the results of experiments should be foretold, and the conclusions to be drawn explicitly stated; it creates a better atmosphere, so to speak, and makes more impression upon the young student's mind, if he is trusted to discover, for example, that a solution of soda is alkaline to litmus, rather than directed to verify the fact. The danger of making too great demands upon his powers of observation and reasoning must, of course, be kept in mind, but unless a book is intended mainly for those who have no instructor it would seem preferable to give too little than too much help.

## CORRESPONDENCE.

### PURIFYING MERCURY IN THE LABORATORY.

*To the Editor of the Chemical News.*

SIR,—In Professor Estreicher's letter, in your issue of Dec. 1st, 1911 (civ., p. 269), he mentions a Dr. Palmaer's funnel, which appears to be rather a good thing. I ordered one immediately after seeing this letter, but our chemical dealer here, in Middlesbro', has not been able to get one for me. Can you help me in the matter? Do any of the London dealers stock them?

WELDON HANSON.

### THE CHANCES OF THE ENGLISH CHEMIST.

*To the Editor of the Chemical News.*

SIR,—In view of the letter published in the *CHEMICAL NEWS*, civ., p. 318, the following facts regarding the treatment of its assistant chemists by a large company may be of interest to your readers.

We have to commence work at 7.30 a.m. and do not finish till 5.15 p.m., with one hour for lunch, and with only seven days' leave per annum. For this our average salary works out at about 6d. per hour, which is 1d. per hour more than a labourer's wages in the yard. In addition, we are not paid for overtime, and casual leave is seldom granted.

We are forbidden to depart from any method laid down in the method book, notwithstanding that many are obsolete and quite useless at the present day, and originality is discouraged by the fact that each group of four assistants is in charge of a senior chemist, who is usually fresh from college and totally ignorant of technical methods of analysis. In addition to the above we are subject to a system of penalties for petty offences, such as is only practised at a school.



Now, sir, I contend that in view of the long and expensive training we have had this treatment is scandalous, and tends to the degradation of analytical chemistry as a profession. If chemists in routine laboratories would only combine to boycott firms of this description a great deal could be done to improve this state of affairs.—I am, &c.,

"ROUTINE."

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. cliii., No. 23, December 4, 1911.

**Europous Chloride.**—G. Urbain and F. Bourion.—Anhydrous europic chloride can be prepared by drying the hydrated chloride at 100° and subjecting it to the action of a current of chlorine and sulphur dichloride, meanwhile gradually raising the temperature. The reduction of europic chloride by hydrogen leads to the formation of the lower chloride  $\text{EuCl}_2$ . It is a white amorphous-looking substance which gives an opalescent neutral solution with cold water. When this solution is concentrated at 100° it undergoes decomposition, according to the equation  $12\text{EuCl}_2 + 3\text{O}_2 = 8\text{EuCl}_3 + 2\text{Eu}_2\text{O}_3$ .

No. 24, December 11, 1911.

**Catalytic Preparation of Alcoholic Amines.**—Paul Sabatier and A. Mailhe.—The direct action of ammonia gas in presence of thorium on various secondary alcohols, and on cyclohexanol and its homologues, gives primary and secondary amines. If the ammonia is replaced by a primary amine a good yield of secondary mixed amine is obtained.

**Stability of Various Types of Smokeless Powders towards Ultraviolet Rays.**—Daniel Berthelot and Henry Gaudechon.—The authors have examined the action of ultraviolet light upon powders of two different types—B-powders and those containing nitroglycerin (ballistites, cordites, &c.). They all underwent rapid decomposition, yielding  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{N}_2$ ,  $\text{N}_2\text{O}$ , and  $\text{NO}$ . The B-powders resisted the action of the rays better than the nitroglycerin powders. Thus the ultraviolet rays provide a new and accurate method of investigating smokeless powders, and particularly of determining their stability when heated.

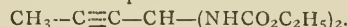
**Compound of Ferric Sulphate and Alcohol.**—A. Recoura.—Ferric sulphate can exist in five forms, four of which are soluble in alcohol. Of these four modifications only one is dissolved rapidly. Its composition is  $\text{Fe}_2\text{SO}_4 \cdot 9\text{H}_2\text{O}$ . When it is kept at 100° it turns yellow and loses 6 molecules of water, undergoing a molecular transformation; it then behaves as if it contained two hydroxyls of acid function, its formula being  $\text{Fe}_2\text{SO}_3(\text{OH})_6$ . Thus in constitution and properties it resembles the green sulphate of chromium,  $\text{Cr}_2\text{SO}_4 \cdot 5\text{H}_2\text{O}$ , but differs from it, firstly, in being able to fix only 1 molecule of sulphuric acid instead of 3, and secondly, in its power of combining with 2 molecules of alcohol, giving a compound the alcoholic solution of which leaves  $\text{Fe}_2\text{SO}_4 \cdot 2\text{H}_2\text{O} \cdot 2\text{C}_2\text{H}_6\text{O}$  on evaporation.

**Formation and Decomposition of Anhydrous Substances.**—Marcel Guichard.—The action of heat upon a hydrated compound usually results in the following phenomena:—(i.) Removal of the combined water, and occlusion or adsorption of part of this water by the anhydrous substance. (ii.) Removal of the adsorbed water. (iii.) Decomposition of the anhydrous substance and occlusion or adsorption of a part of the gaseous products of decomposition by the solid residue. (iv.) Removal of

the adsorbed substances. Thus, in order to prepare a perfectly pure anhydrous substance the combined water must be eliminated, and also the adsorbed water at a temperature at which the anhydrous substance does not begin to decompose. In the case of iodic acid the temperature at which the water is eliminated is close to the temperature at which the anhydride decomposes. If the anhydride is heated to 250° *in vacuo* for 100 hours the amount of decomposition is negligible, and only very minute traces of water are retained.

**Action of Monochlorurea on Ketones.**—A. Béhal and A. Detœuf.—Monochlorurea readily acts on ketones, giving, if equimolecular weights are employed, monochloro-derivatives. The chlorine always attaches itself to the ketone function, yielding only one derivative if the ketone molecule is symmetrical, and two if it is asymmetrical. In the latter case the secondary carbon is attacked more easily than the primary carbon. The chloro-derivatives give chlorinated semicarbazones with semicarbazide.

**Derivatives of Tetrolic Aldehyde and of its Acetal.**—P. L. Viguier.—The action of aniline on tetrolic aldehyde gives a substance of formula  $\text{CH}_3\text{—C}(\text{NHC}_6\text{H}_5) = \text{CH—CH} = \text{NC}_6\text{H}_5 \cdot \text{HCl}$ . With phenyl hydrazine viscous liquids are obtained, which on distillation yield 1-phenyl-5-methylpyrazol. Urethane gives the condensation product—



Alcohol readily condenses with tetrolic acetal, the product being  $\beta$ -ethoxycrotonic acetal.

*Berichte der Deutschen Chemischen Gesellschaft.*

Vol. xlv., No. 17, 1911.

**Thiophosphates and Thiophosphites.**—Fritz Ephraim and Rebecca Stein.—Potassium tetrathiosulphate can be prepared by heating together 100 grms. of crystallised potassium sulphide and 7.5 grms. of phosphorus pentasulphide. Its formula is  $\text{K}_3\text{PS}_4 \cdot \text{H}_2\text{O}$ . Ammonium tetrathiosulphate is obtained by saturating ice-cold aqueous ammonia with  $\text{H}_2\text{S}$  and  $\text{NH}_3$ , and adding phosphorus pentasulphide. Barium tetrathiosulphate,  $\text{Ba}_3(\text{PS}_4)_2 \cdot \text{aq.}$ , and strontium trithiosulphate,  $\text{Sr}_3\text{H}_6(\text{PS}_3\text{O})_4 \cdot \text{aq.}$  are formed by the double decomposition of the corresponding hydroxides with sodium tetrathiosulphate. Metallic sulphides in aqueous solution react with  $\text{P}_4\text{S}_3$  and  $\text{P}_4\text{S}_7$ . In the case of sodium sulphide the products have the formula  $\text{Na}_3\text{PS}_3 \cdot \text{aq.}$ , and appear to differ only in the amounts of water of crystallisation they contain. The products appear to be thiophosphites. Barium sulphide with  $\text{P}_4\text{S}_7$  yields barium trithiosulphite,  $\text{Ba}_3(\text{PS}_3)_2 \cdot \text{aq.}$ , and with  $\text{P}_4\text{S}_3$  barium-oxy-thiophosphite,  $\text{Ba}_3(\text{PS}_3\text{O})_2 \cdot 8\text{H}_2\text{O}$ .

**Diamido-thiophosphoric Acid.**—Fritz Ephraim.—Diamido-thiophosphoric acid can be prepared from the dichloride  $\text{POC}_6\text{H}_5$  by warming it with sulphur, replacing the chlorine atoms by the amido groups by means of the action of ammonia, and finally saponifying the phenyl ester. The free acid is an oil which is very unstable, readily giving off sulphuretted hydrogen. It gives a characteristic white silver salt, which is precipitated from even a very dilute solution.

**Hydrazido-phosphoric Acid.**—Fritz Ephraim and M. Sackheim.—The chloride of phosphoric acid diphenyl ester is readily converted into the corresponding hydrazide by the action of hydrazine, and on saponification salts of free hydrazido-phosphoric acid are obtained. The free acid cannot be isolated in the pure state, but is stable in aqueous solution. It gives two series of salts, the properties of which are very similar to those of amidophosphoric acid.

**Iodine Oxides and Iodic Nitrate.**—H. Kappeler.—The author has endeavoured to prepare the supposed oxides  $\text{I}_2\text{O}_{10}$  and  $\text{I}_6\text{O}_{13}$ , following the directions of their

discoverers, and has come to the conclusion that they are both identical with the basic iodi-iodate  $I_2O_4$ . Yellow iodic nitrate is obtained by oxidising iodine with very concentrated nitric acid ( $d = 1.52$ ). The ordinary concentrated acid ( $d = 1.4$ ) does not attack iodine in the cold, and nitric acid of density 1.48 only oxidises it to iodic acid. The yellow substance is probably the basic nitrate  $IO(NO_3)$ .

*Bulletin de la Société Chimique de France.*  
Vol. ix.-x., No. 23, December 5, 1911.

**Solutions and Dissolved Particles.**—Albert Colson. — From a study of the dissolved particle of acetic acid the author concludes that the identification of the osmotic and gaseous particles with the particles expressed by the condition  $R = \rho$  is absolutely contrary to the true facts, since Avogadro's hypothesis and its kinetic consequences are not satisfied by the dissolved particles although they always are satisfied by the gaseous molecules, whether condensed or not.

**Osmotic Pressure.**—Maurice Prud'homme. — The author in this paper puts forward a theory of molecular attraction according to which the pressure exerted by the molecules of a dissolved substance in a certain volume of a solvent is equal to the attraction of the molecules for those of the solvent. This hypothesis enables the laws of osmotic pressure to be deduced *a priori*, and the laws of the lowering of the vapour tensions of solutions and of the diffusion of dissolved substances are also readily established.

**Alloys of Cobalt and Zinc.**—F. Ducelliez. — By chemical methods the compound  $CoZn_4$ , containing 81.6 per cent of zinc, can be isolated from alloys of cobalt and zinc containing more than 81.6 per cent of zinc. This percentage corresponds to the limit of magnetism of these alloys, and the study of the electromotive forces of the alloys also demonstrates the existence of the same compound.

**New Dodecane.**—M. Delacre. — When sodium acts on the HBr addition product of pseudo-butylethylene which has not been freed from pseudo-butylacetylene a compound is obtained which boils at  $185^\circ$ . This compound appears to be the new dodecane,  $(CH_3)_3C \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot C(CH_3)_3$ . It is a colourless liquid, frequently containing needle-like crystals which disappear on warming in the hand. It has a faint aromatic odour. Towards bromine it behaves like a saturated compound.

**Action of Sodium Hypochlorite on Hexamethylene-tetramine.**—Marcel Delépine. — When commercial sodium hypochlorite containing 4 to 5 per cent of active chlorine acts on an aqueous solution of hexamethylene-amine, shining lamellæ of dichloropentamethylene-tetramine are deposited. It is a fairly stable product, which can be kept for some days without undergoing any alteration. It dissolves very rapidly in eight or ten times its weight of acetic acid, giving symmetrical trichlorohexahydrotriazine,  $C_3H_6N_3Cl_3$ .

## MISCELLANEOUS.

**Philippine Journal of Science.**—On account of a change in paper and type, No. 1, vol. vii., 1912, of the *Philippine Journal of Science* will not be published before March, 1912.

**Photographs.**—A collection of pictorial photographs is now on view at the house of the Royal Photographic Society, 35, Russell Square, from January 24th till February 24th, and is open free to the public on presentation of visiting card. The photographs are by Members of Societies affiliated to the Royal Photographic Society, and have been selected as being the best work produced by each Society. None who are interested in the cultivation of artistic taste in photographic work should fail to see this collection.

**Association of Chemical Technologists.**—A meeting of the London Section of the above Association will be held on Friday, January 26th, at 8 o'clock, at St. Bride's Institute, Bride Lane, Fleet Street, E.C., when a paper will be read by Mr. J. W. Hinchley, A.R.S.M., Wh.Sc., on "Works Management."

**Royal Institution.**—On Thursday next, February 1st, at 3 o'clock, Prof. A. M. Worthington begins a course of two experimentally illustrated lectures at the Royal Institution on "The Phenomena of Splashes," and on Saturday, February 3rd, Sir Alexander C. Mackenzie delivers the first of a course of lectures, with musical illustrations, on (1) "Russian Music of To-day" (with the kind assistance of the Hans Wessely Quartet), and (2 and 3) "Franz Liszt Centenary." The Friday evening discourse, on February 2nd, will be delivered by Sir James Mackenzie Davidson on "Vital Effects of Radium and other Rays," and on February 9th, by Dr. J. A. Harker, on "Very High Temperatures."

**Institute of Chemistry.**—Past List, January Examinations, 1912.—Of twelve Candidates who presented themselves for the Intermediate Examination seven passed—R. M. Doidge, B.Sc. (Lond.); D. R. Frazer; S. G. Greene; G. S. Heaven, B.Sc. (Lond.); W. Honneyman; A. Wilson; and T. Wright. Of fifteen Candidates who presented themselves for the Final Examination eleven passed:—In the Branch of Mineral Chemistry—E. C. Evans, B.Sc. (Wales); H. W. Moss, A.R.C.Sc.1.; and N. C. Nag, M.A. (Calcutta); in the Branch of Organic Chemistry—D. Cardwell, B.Sc. (Manc.), H. Krall, B.A. (T.D.C.), F. H. Lees, and W. M. Roberts, B.Sc. (Manc.); in the Branch of the Chemistry of Food and Drugs, and of Water—G. D. Elsdon, B.Sc. (Birm.), H. Hawley, M.Sc. (Birm.), R. L. Morris, and F. G. C. Walker.

## MEETINGS FOR THE WEEK.

MONDAY, 29th.—Royal Society of Arts, 8. (Cantor Lecture). "Ocean Waves, Sea-beaches, and Sandbanks," by Vaughan Cornish, D.Sc.

TUESDAY, 30th.—Royal Institution, 3. "The Study of Genetics," by Prof. W. Bateson, F.R.S.

— Royal Society of Arts, 4.30. "Irrigation in South Africa," by W. A. Legg, M. Inst.C.E.

WEDNESDAY, 31st.—Royal Society of Arts, 8. "Recent Progress in Radio-telegraphy," by Prof. G. W. Osborn Howe, M.Sc.

THURSDAY, Feb. 1st.—Royal Institution, 3. "Phenomena of Splashes," by A. M. Worthington.

— Royal Society. "Bacterial Production of Acetyl-methylcarbinol and Butylene Glycol from various Substances," by A. Harden and Miss D. Norris. Distribution of the Nerves of the Dental Pulp," by J. H. Mummery. "Method for Isolating and Cultivating the *Mycobacterium Pseudo Tuberculosis enteritidis bovis johne*, and some Experiments on the Preparation of a Diagnostic Vaccine for Pseudo-tuberculous Enteritis of Bovines," by F. W. Twort and G. L. Y. Ingram. "Fossil Flora of the Forest of Dean Coalfield (Gloucestershire), and the Relationship of the Coalfields of the West of England and South Wales," by E. A. N. Arber. "Chemical Action of *Bacillus Cloacæ* (Jordan) on Glucose and Mannitol," by J. Thompson. "Simultaneous Colour Contrast," by F. W. Edridge Green.

— Chemical, 8.30. "Constituents of Commercial Chrysarobin," by F. Tutin and H. W. B. Clewer. "Researches on Bleaching Powder—Part II., The Action of Dilute Acids on Bleaching Powder," by R. L. Taylor and C. Bostock. "The Quantitative Estimation of Hydroxy-, Amino-, and Imino-derivatives of Organic Compounds by means of the Grignard Reagent, and the Nature of the Changes taking place in Solution," by H. Hibbert. "An Exact Investigation of the Three-component System—Sodium Oxide, Acetic Anhydride, Water," by A. C. Dunningham.

FRIDAY, 2nd.—Royal Institution, 9. "Vital Effects of Radium and other Rays," by Sir James Mackenzie Davidson, M.B., &c.

SATURDAY, 3rd.—Royal Institution, 3. "Russian Music of To-day," by Sir Alexander C. Mackenzie, Mus. Doc., &c. (with the kind assistance of the Hans Wessely Quartet).



# THE CHEMICAL NEWS.

VOL. CV., No. 2723.

## THE INTRODUCTION OF PHYSICAL CHEMICAL CONCEPTIONS IN THE EARLY STAGES OF THE TEACHING OF CHEMISTRY.\*

By HARRY C. JONES.

(Concluded from p. 38).

AND now we come to another fundamental matter—the nature of the units that take part in chemical reaction. For a long time it was taught that the atoms and the molecules are the active chemical agents, and this was in keeping with what was known at the time.

This is now largely changed. The number of concordant lines of evidence which show that electrically charged parts are necessary for chemical activity is so great, that I know of no productive chemist to-day who seriously questions it. After thinking over this problem and working upon it for a good many years, I am of the opinion that there is no chemical reaction known to man in which at least one of the substances taking part in the reaction is not more or less ionised. Indeed, I am unable to form any physical conception of even the possibility of a chemical reaction between electrically neutral parts any more than I can form a conception of two electrically neutral bodies attracting or repelling one another electrically. It would lead us much too far to discuss at all fully this question here, nor is it necessary to do so. To furnish evidence to-day for the general truth of the theory of electrolytic dissociation would be as unwise and as useless as to furnish new evidence for the law of the conservation of energy, or the law of the conservation of mass.

In the light of these facts are we justified in continuing to teach the beginner the old chemistry of atoms and molecules which we know, or should know, is untrue, trusting to later years, to new experiences, or to another instructor to correct these erroneous first impressions, which, as has been stated, is well nigh impossible.

Take another phase of things. A phenomenon which must be encountered very early in the study of chemistry is *precipitation*, already referred to in another connection. Has it been possible to treat this subject scientifically until quite recently? I think not. Whenever a precipitate could be formed it was formed, was about the way this matter was left. In the chemical reaction in question a solid is formed, which is practically insoluble in the solvent used, and being insoluble it is thrown down in that coarse-grained condition that we call a precipitate.

Think of this for a moment. When the solid was formed it was probably in a state of molecular aggregation. How do these solid molecules know enough to come together and form aggregates of the sizes that exist in precipitates? Furthermore, if this is the "natural condition" of insoluble solids when formed in a chemical reaction, then why do we not *always* have precipitation when an insoluble solid is formed in a reaction? In a word, why do we have, in some cases, *colloidal suspensions*?

To fix the idea, and by way of illustration, why is arsenic sulphide precipitated when arsenic chloride is treated with hydrogen sulphide, but is not precipitated when arsenic oxide of the same concentration as the chloride is treated with hydrogen sulphide? Not only must every teacher of chemistry have asked himself this question, but every intelligent student, before he has advanced very far, must do so.

This is now very satisfactorily explained by another really great man of science—a man whose work for chemistry is quite as fundamental as his work for physics—I refer, of course, to Sir J. J. Thomson.

He has shown that whether or not precipitates are formed is dependent upon the presence or absence of appreciable numbers of charged parts or ions. Arsenic sulphide is precipitated from the solution of the chloride because the hydrochloric acid set free by the action of the hydrogen sulphide is strongly ionised. On the other hand, arsenic sulphide is *not* precipitated from the solution of the oxide, because no strongly dissociated substance is formed as the result of the reaction, and neither arsenic oxide or hydrogen sulphide is strongly dissociated.

But Thomson does not stop with showing that ions or charged parts are necessary for precipitation. It was shown by Burton, working in Thomson's laboratory, why, or at least how, this is the case. Space will not allow me to go into this in detail. Suffice it to say here that the colloiddally suspended particles are charged electrically, and for any given colloid all of the particles are charged with the same sign. These electrical repulsions work counter to surface-tension, which acts so as to draw the particles into the smallest surface for a given mass—to draw the colloiddal particles into lumps as in an ordinary precipitate. When ions are present these electrically neutralised the charges upon the colloiddal particles, and allow surface-tension to produce its full effect.

That ions are necessary and sufficient to effect precipitation can readily be shown by adding almost any electrolyte to the colloiddally suspended particles of arsenic sulphide, obtained by treating the oxide with hydrogen sulphide. A precipitate is formed at once.

This work places the whole subject of precipitation, for the first time, upon a scientific basis, and while it cannot be presented fully to a beginner, I see no reason why it should not be judiciously taught to a student in his second year of chemistry, *i.e.*, when he is studying qualitative and quantitative analysis.

Then arise some of the most fundamental problems. What is a chemical atom? If made up of parts what are these parts, and how are they arranged within the atom? How does one chemical atom differ from another chemical atom? Are the chemical atoms stable?

These matters must all be taught the student of chemistry, and the question is when? They cannot, of course, all be presented fully to what we ordinarily mean by a beginner, but I can see no reason why they cannot be presented, in an elementary manner, of course, in outline at the proper places, even in the first year's work in chemistry, unless we are wedded to the dogma that chemistry must be made *easy* in order that it may be *popular*.

We can certainly no longer teach that the chemical atom is an "ultimate unit" in the light of the recent work of Thomson. We know that it is made up of parts, and, furthermore, we have some idea how these parts are arranged in two dimensions in space in a section through the atom. We have very good reason to believe that most, if not all, of the differences between the atoms of the various chemical elements are a function of the number, arrangement, and possibly the velocities of the electrons composing the atoms. And why not, in a common sense manner, tell the student of chemistry so, even in the comparatively early stages of his work?

Indeed, I think it is far simpler to teach this fundamental connection between the elements, than to have the beginner look upon the eighty or more elementary substances as so many discrete, disconnected, and fundamentally unrelated kinds of matter, to say nothing of it being true, and in the teaching of science I think *truth* is even more important than *simplicity*.

And again, take the question of the *stability* of the chemical atom. The stable atom of the past is now hardly more than historically interesting. The work of the Curies, and especially of Rutherford, on radioactive substances, has

\* Read before the American Chemical Society in Washington, December 27th, 1911.

placed this almost beyond the pale of doubt. The atoms with the largest atomic masses are certainly unstable, and it is highly probable that the atoms of all the elements are undergoing evolutionary changes.

In the light of these facts are we going to persist in teaching the stable atom without qualification, even to the beginner, and rely upon time, fate, or the effort of some one else to correct, if possible, the evil that we have done? It is perfectly true that the stable atom is simpler for the beginner than the unstable atom, but here again it is *simplicity versus truth*.

In conclusion, there is one other matter which I cannot leave untouched, because it lies at the very foundation of our science. I submit that no serious student of chemistry, and this is the class for which we must be most concerned, can study the subject for six months, learning that certain things react chemically with certain other things, and that certain things do not react with one another, without asking himself the question, why is this? Why do some substances react, and why do others not react? If this question is not raised by the student it certainly should be by the instructor. The question then is, why do chemical reactions take place at all?

We might almost call this the most fundamental question of chemical science. It is certainly so for the student, and that in the early part of his career.

This brings me to the most heterodox position that I have yet ventured to take.

Should we not introduce into our elementary courses in chemistry something about the *energy changes* that take place in all chemical reactions, and which make those reactions possible? In the evolution of chemistry the material changes were studied first, and this was natural. These changes were the most obvious, and the material products were often desired for one purpose or another. Again, these material changes were the easiest to study, and chemists, like other men, were inclined to follow the lines of least resistance. I believe the nineteenth century will go down in the history of chemistry primarily as the period of *material chemistry*.

But even this is changed now. Without decrying in the least the study of matter, the chemist of to-day insists that we can no longer ignore the changes in energy that manifest themselves in every chemical reaction. Indeed, he would go even further, and point out again that whatever is easiest in science is relatively most superficial.

We know to-day that *all* chemical reactions are due to differences in the intensity, or quantity, or kind of the intrinsic energy present in the substances that are to react, and whether any two substances will react or not is determined primarily by these differences. We can furthermore form a physical conception now of what is meant by intrinsic energy, since we have the electron theory of the atom; it is primarily the kinetic energy of the moving electrons within the atom.

But dare we venture even to refer to energy or energy changes in the early stages of the teaching of chemistry? I ask, why not? The physicist does not hesitate to do so. Indeed, most of his subject has to do very largely with changes in the different manifestations of energy. Why should we assume that the chemical student has less natural intelligence than the student of physics, especially when he is almost always the same student? (In my opinion no one should be allowed to begin the study of chemistry until he has had at least one year of physics.)

There is, of course, no reason for assuming that the beginning chemist is not as intelligent as the beginning physicist, and, therefore, there is no more reason why a student of chemistry should not deal with changes in energy than a student in physics, especially when these energy changes are as fundamental for chemical science as they are for physics.

Instead of teaching to-day that chemical reactions are accompanied by energy changes, why not teach the truth, which is that it is these very energy changes that are the cause of all chemical reaction? Systems which alone are

fairly stable when brought together may become unstable. There is a running down of a part of the intrinsic energy of one or both of the substances into heat, light, or electricity, but almost always largely into heat, and the substances rearrange themselves into those new combinations which are most stable under the new conditions.

This is what we ordinarily describe as a chemical reaction, and this can be taught to any sensible student just as well as the elements of physics can be taught him.

Finally, the matters herein referred to, together with many others, which time will not permit me even to mention, cannot, of course, be taught the beginner all at once, in addition to the so-called material facts of chemistry. It is, however, a fair question to ask whether some of these matters would not be a fair substitute for a part of the pyrotechnics that sometimes adorn the chemical lecture table?

In all such matters the judgment and common sense of the teacher must of course be the final guide, and the intellectual fibre of the student must also be taken into account. It goes without saying that we must not teach dogmatically anything to the student of chemistry, much less to the beginner in chemistry, that is not reasonably substantiated; but I believe that all of the matters referred to above and many more of their type belong in this class.

The final question then is, shall we have two chemistries or one? Shall we have a chemistry of research, pushing forward at a pace that makes the last twenty-five years mark a distinctly new epoch in the history of the science, and another chemistry taught the beginner, which practically ignores all that has been done within that period, which deals not only with what is obsolete, but with what in part we know to be untrue, and which relies upon subsequent teaching to do almost the impossible, *i.e.*, correct erroneous first impressions, which must by some method be corrected, or the result is fatal?

Or shall we have one science of chemistry, research leading the way, and teaching following fairly closely behind, at least doing nothing that will have to be undone, but incorporating what is truest and best?

For those who believe, as I do, that the latter is the more scientific course, there is not only no ground for pessimism, but not even for pragmatic meliorism.

The progress in this direction during the last decade, not only in the better colleges and universities, but in the more progressive high schools, has been so rapid that there is room for nothing but the most cheerful optimism.

## TRANSFORMATION OF OTHER FORMS OF CARBON INTO GRAPHITE.\*

By W. C. ARSEM.

(Concluded from p. 40).

### Experimental Methods.

ALL samples were ground to fine powder before firing to facilitate the determination of specific gravity, and all samples were tested, after firing, by treatment with potassium chlorate and nitric acid.

*Grinding.*—To insure freedom from enclosed air, which would vitiate the specific gravity results, all samples of carbon were ground in a roller-mill. This is a steel cylinder with a tightly fitting cover on each end, and contains four steel rolls. All the surfaces are case-hardened and polished, to insure a minimum of wear. As to the extent to which iron is introduced, it is found that after fifty hours grinding of a 20-grm. sample of petroleum coke, the ash had increased only 0.09 per cent. The mill is rotated at 200 r.p.m., and from two to eight hours is sufficient to grind most substances, so that the largest particles are not over 0.005 mm. in diameter.

\* From the *Chemical Engineer*, xiv., No. 4.



**Firing.**—The samples were packed in small Acheson graphite crucibles with tightly fitting covers. These, in turn, were placed in larger tubular graphite crucibles, closed at both ends, the space between the smaller and larger crucibles being packed with Acheson granular graphite, previously fired, and containing only mere traces of ash. The samples thus protected were fired at approximately 3000° to 3300° C. in an experimental tube furnace for fifteen minutes. This furnace consisted of a heater tube of Acheson graphite surrounded by an insulated carbon tube with an annular free space between them. The outer carbon tube is well packed in granular petroleum coke, but no packing material is in contact with the heater. With the exception of the graphite heater tube, which was renewed for each run, the furnace has been used for a great many runs, and is practically free from metallic impurities.

When making tests of purified and unpurified samples of the same kind of carbon, the purified samples were always fired in a tube which had not previously been used for firing impure carbon.

**Specific Gravity.**—Specific gravity determinations were made on samples pulverised as above stated, using a pyknometer of the form shown in Fig. 1, holding about 7 cc. The sample was weighed in the pyknometer, which

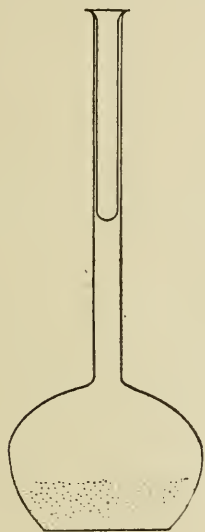


FIG. 1.

was then half filled with Kahlbaum's chemically pure benzene, and heated to the boiling-point of the benzene to remove air and fill the pores of the carbon. Owing to the fineness of the powder this can be accomplished in a few minutes. The pyknometer was then cooled to 20° C., filled to the mark with benzene, and weighed. Results are referred to water at 4° C. The limit of accuracy is about 0.005.

**Brodie's Test.**—All samples before and after firing were tested by Brodie's method, which consists in heating the sample with fuming nitric acid and potassium chlorate. "Amorphous Carbon" is converted into brown soluble substances, while graphite is changed to green graphitic oxide, or yellow graphitic acid, according to the concentration of the nitric acid or the duration of the treatment.

In my experiments I used in some cases nitric acid, distilled from a mixture of concentrated nitric and sulphuric acids. In other cases the nitric acid was made by distilling well dried potassium nitrate with concentrated sulphuric acid, as recommended by Moissan.

### Experimental Results.

**Petroleum Coke.**—This was obtained from the Standard Oil Company in lump form, and contained 0.10 per cent ash. These lumps, when fired, had all the physical properties of graphite, being soft and of a silver-grey colour. They marked paper easily. A sample of this graphite, pulverised before firing, had a specific gravity of 2.26. This value was checked a number of times. A sample of the coke ground with 5 per cent ferric oxide had a specific gravity after firing of only 2.22.

It is thus seen that quite pure petroleum coke, when fired without additions, yields a very good grade of graphite and that the addition of iron oxide is, if anything, disadvantageous.

**Bituminous Coal Coke.**—This was ordinary foundry coke, containing about 10 per cent of red ash, mostly iron and silica.

Lumps of this coke, when fired, became bright grey, and gave the characteristic grey streak on paper. This material seemed harder than petroleum coke graphite. Some of the powdered coke, when fired, had a specific gravity of 2.192.

A sample was treated with fused sodium hydroxide, then with water, and finally with hydrochloric acid. The ash was now reduced to 5.70. After firing, its specific gravity was 2.225.

The results of these experiments are given in Table II.

TABLE II.

|                                                | Ash before firing. | Ash after firing. | Sp. gr. after firing. |
|------------------------------------------------|--------------------|-------------------|-----------------------|
| Crude coke . . . . .                           | 10.00              | 2.07              | 2.192                 |
| Treated with fused NaOH, then with HCl . . . . | 5.70               | 0.78              | 2.225                 |

Here we see again the *smaller* the amount of mineral matter present, the *higher* the specific gravity reached on firing.

**Anthracite Coal.**—A sample of Lackawanna coal, containing 6.46 per cent ash when fired in lump form came out bright grey, rather hard, and with a tendency to cleave into plates and angular fragments, like the unfired coal. It marked paper with some difficulty, and its feel and appearance were much less graphite than in the case of the fired foundry coke and petroleum coke.

A pulverised sample, when fired, had a specific gravity of 2.133.

Some of the pulverised coal, when treated with fused NaOH, then washed and treated with HCl, had its ash reduced to 0.20 per cent, and this purified coal when fired had a specific gravity of 2.149, a value slightly higher than that given by the crude coal.

To check this result some samples of coal obtained from the U.S. Geological Survey were treated in the same way. The results were even more striking, as may be seen from Table III.

TABLE III.—Results of Firing Anthracite Coal above 3000°.

| Coal samples.                                    | Ash before firing. | Ash after firing. | Sp. gr. after firing. |
|--------------------------------------------------|--------------------|-------------------|-----------------------|
| Lackawanna (crude) . . . .                       | 6.46               | —                 | 2.133                 |
| Lackawanna (purified) . .                        | 0.20               | —                 | 2.149                 |
| U. S. G. S. "Buckwheat No. 1" (crude) . . . .    | 17.68              | —                 | 2.125                 |
| U. S. G. S. "Buckwheat No. 1" (purified) . . . . | 1.73               | —                 | 2.170                 |
| U. S. G. S. "Buckwheat No. 5" (crude) . . . .    | 13.30              | —                 | 2.138                 |
| U. S. G. S. "Buckwheat No. 5" (purified) . . . . | 0.93               | —                 | 2.180                 |

Anthracite coal, therefore, is a form of carbon which graphitises only imperfectly, in spite of the high percentage of ash, which is well distributed throughout the material. We have here, therefore, excellent conditions for catalytic action without a corresponding effect. The results show that the presence of ash *hinders* rather than

assists graphitisation. Some samples of coal seem to yield purer graphite than others, especially after the ash has been removed.

**Lampblack.**—A commercial variety of lampblack, known as "Patton's Sunproof," containing about 0.2 per cent ash, principally iron oxide, when fired in the tube furnace reached a specific gravity of 2.090. Some of the lampblack, unfired, was ground with 5 per cent ferric oxide and fired. This had a specific gravity of 2.094. Another sample of lampblack was impregnated with ferric oxide, so as to obtain as good a distribution as possible in the following way:—

The lampblack was stirred into a solution of ferric chloride, and ammonia was added to precipitate ferric oxide, forming an apparent homogeneous mixture. This mixture was well dried, and divided into two portions; the first was heated one hour *in vacuo* at 1600°, and the other one hour at 2000° to reduce the iron oxide to metal, and then both were fired in the graphite tube furnace at about 3300°. After firing, the specific gravity of the first portion was 2.122, and of the second portion 2.109. All these fired samples were indistinguishable from each other by physical or chemical tests. We have here a pure form of carbon which reaches a limiting density of about 2.10, and this limit is not appreciably raised by the presence of even 5 per cent ferric oxide, although the distribution of the latter was about as perfect as possible and the conditions especially favourable for a catalytic transformation into a more graphitic variety of carbon if this were possible. They are all greyish black non-crystalline powders. They all yield by Brodie's test a yellow graphitic acid, but have none of the characteristic properties of graphite.

Another sample of lampblack, Reichard's No. 7, was also fired, and reached a density of 2.074.

Patton's sun-proof lampblack was also heated with small percentages of different substances, but no catalytic effect was noticeable.

The results are summarised in the table:—

|                                                                                             | Density. |
|---------------------------------------------------------------------------------------------|----------|
| Patton's lampblack, 0.2 per cent ash .. .. .                                                | 2.090    |
| Patton's lampblack + 5 per cent Fe <sub>2</sub> O <sub>3</sub> ground together .. .. .      | 2.094    |
| Patton's lampblack + 5 per cent Fe <sub>2</sub> O <sub>3</sub> by precipitation (a) .. .. . | 2.122    |
| Patton's lampblack + 5 per cent Fe <sub>2</sub> O <sub>3</sub> by precipitation (b) .. .. . | 2.109    |
| Patton's lampblack + 5 per cent Al <sub>2</sub> O <sub>3</sub> .. .. .                      | 2.080    |
| Patton's lampblack + 1 per cent Si .. .. .                                                  | 2.076    |
| Patton's lampblack + 5 per cent MnO <sub>2</sub> .. .. .                                    | 2.091    |
| Patton's lampblack + 5 per cent NiO .. .. .                                                 | 2.099    |
| Reichard's lampblack .. .. .                                                                | 2.074    |

**Retort Carbon.**—The carbon obtained from the inside walls of gas retorts occurs in three varieties, black, grey, and white. These differ in ash content and in behaviour on heating, and show in a striking way that the ability to graphitise is independent of the amount of ash present. Both the white and the grey varieties yield excellent graphite, although the former is very low in ash and the latter high.

The black variety which is also in ash does not graphitise, but reaches a density of 2.11. Four different substances tried as catalysts had no effect, the density after firing being practically the same as that of the same carbon fired without mineral additions. (See Table IV.).

**Diamond.**—Some white diamonds when fired became converted into a coke-like carbon, having a specific gravity of 1.915, which does not mark paper.

Parsons and Swinton heated a diamond in the focus of a cathode ray tube at 1890° (*Proc. Roy. Soc.*, 1908, lxxx., 184), and state that it was converted into coke. The specific gravity was not stated.

These results are especially interesting since it has been commonly supposed that the diamond is converted into

TABLE IV.—Effect of Heating Retort Carbon above 3000°.

|                                                                          | Ash before firing. | Ash after firing. | Sp. gr. after firing. |
|--------------------------------------------------------------------------|--------------------|-------------------|-----------------------|
| White retort carbon .. .. .                                              | 0.34               | 0.10              | 2.265                 |
| Grey retort carbon .. .. .                                               | 2.66               | 0.16              | 2.263                 |
| Black retort carbon .. .. .                                              | 0.23               | 0.10              | 2.116                 |
| Black retort carbon + 1 per cent CaO .. .. .                             | —                  | 0.31              | 2.123                 |
| Black retort carbon + 1 per cent SiO <sub>2</sub> .. .. .                | —                  | 0.12              | 2.117                 |
| Black retort carbon + 1 per cent Li <sub>2</sub> CO <sub>3</sub> .. .. . | —                  | 0.05              | 2.129                 |
| Black retort carbon + 2 per cent Fe <sub>2</sub> O <sub>3</sub> .. .. .  | —                  | 0.09              | 2.178                 |

graphite by heat, and statements to that effect appear in most text-books.

#### Conclusions.

All the pure forms of carbon which have been tested, when fired above 3000°, reach a limiting density which is not appreciably raised by the addition of small amounts of mineral matter. The end product is graphite in some cases and not in others. Pure petroleum coke, heated without addition of mineral matter, is converted into graphite of excellent quality, while lampblack, although it increases in density, does not reach the value corresponding to graphite, nor acquire any of its other physical properties, even when heated with various oxides.

The impure carbons show a similar behaviour. The properties of these carbons after firing are characteristic for each variety of carbon, and independent of the amount of ash present.

Anthracite coal is only imperfectly graphitised by heating. The specific gravity of the fired material was approximately the same for three samples having a range of ash content. Moreover, coal from which most of the ash has been previously removed graphitises better than the crude material.

Bituminous coal coke, which graphitises fairly well, yields an even better product if a part of its ash has been removed before firing.

It must therefore be concluded that a small amount of mineral matter exercises no beneficial effect in the manufacture of graphite by the heating of carbon, and that the quality of the product cannot be improved in this way. As to the effect of mineral matter on the rate of conversion, no data are yet available, although some experimental work along this line has been started. At 3000° the maximum density is reached in less than fifteen minutes for any variety of carbon.

We need some theory of the nature of graphite and of amorphous carbon which will permit a rational explanation of the changes which occur on heating. The following discussion is a tentative step in this direction:—

#### The Nature of Graphite.

Graphite, in the most restricted sense of the term, is an allotropic form of carbon having a definite and not very complex molecular configuration. The molecule might, for example, be regarded as two benzene rings side by side and joined at all six angles, the extra bonds being satisfied as in the usual centric formula. Such a formula might be used to explain the formation of mellitic acid and graphitic acid by oxidation of graphite.

**Amorphous Carbon.**—When an organic compound is decomposed, there results a mixture of substances constantly increasing in complexity until finally carbon is obtained. This carbon need not be regarded as a simple substance, but may be considered to be a mixture of many varieties of carbon, each with a different number and arrangement of atoms in the molecule. According to this view, it seems better not to regard "amorphous carbon" as the name of a distinct allotropic form, but rather as a general term covering all varieties of carbon except



graphite and diamond. In speaking of amorphous carbon, therefore, the source of each sample should be stated.

*The Mode of Transformation.*—In a given sample of amorphous carbon, some of the molecules will be capable of easily undergoing rearrangement under the influence of heat to form graphite molecules, while others will not, and the proportion of molecules capable of such change will determine the character of the final product.

Petroleum coke would therefore consist almost wholly of graphitisable molecules, while anthracite coal contains a smaller proportion.

## CHEMICAL NATURE OF SOIL ORGANIC MATTER.\*

By OSWALD SCHREINER and EDMUND C. SHOREY.

(Continued from p. 42).

### DIAMINO ACIDS (HEXONE BASES).

ALL protein bodies give some diamino acids on decomposition. Three of these occur very frequently, and usually together, but in varying proportions, one predominating in one protein and another predominating in a protein from some other source. These are lysine, arginine, and histidine, all basic compounds, the constitution of which is known. Two of these, arginine and histidine, have been isolated from soils.

#### *Histidine, C<sub>6</sub>H<sub>9</sub>O<sub>2</sub>N<sub>3</sub>.*

Histidine and arginine usually occur together, and the method of their isolation depends on the fact that they are precipitated by silver salts, sulphate or nitrate, from alkaline solution. The solution may be made alkaline with ammonia or barium, but the fact that the histidine silver precipitate is dissolved by a slight excess of ammonia makes the use of barium hydroxide preferable. Separation of the two is accomplished by taking advantage of the fact that histidine silver is precipitated in slightly alkaline solution, while the arginine compound is not precipitated except in strongly alkaline medium. The isolation and separation of these two compounds is then simply two steps in one method. The method in detail is as follows:—

The soil, Houston clay, was treated with 2 per cent sodium hydroxide solution for several hours, the clear liquid syphoned off and acidified with sulphuric acid. In the case of this soil, which was calcareous, the alkaline extract was light coloured, and, on acidifying, the humus precipitate was slight. The acid filtrate was made neutral, and to it, without filtering, silver sulphate in excess was added and then filtered. From this point the method of Kossel and Kutscher was used (*Zeit. Phys. Chem.*, 1900, xxxi., 166). The neutral filtrate was saturated with barium hydroxide, and the precipitate removed and washed with barium hydroxide solution. The precipitate of arginine and histidine silver was then suspended in dilute sulphuric acid and decomposed with hydrogen sulphide. The filtrate from the silver sulphide was then evaporated to a smaller volume, neutralised with barium hydroxide, and barium nitrate added until all sulphuric acid had been precipitated. The filtrate from barium sulphate was then concentrated, and silver nitrate added until a drop added to an excess of barium hydroxide solution gave a yellow precipitate. The solution was then neutralised with barium hydroxide, and the addition carefully continued until a portion of the liquid no longer gave a precipitate with ammoniacal silver nitrate, showing complete precipitation of histidine. The arginine remains in solution.

The histidine silver precipitate, after being filtered off, washed, and suspended in dilute sulphuric acid, was decomposed with hydrogen sulphide. The filtrate from the silver sulphide was freed from sulphuric acid with barium hydroxide, and excess of the latter removed with carbon dioxide.

The filtrate from barium carbonate was evaporated to dryness, taken up with silver nitrate solution and a drop of nitric acid, and filtered from any insoluble matter present. Ammoniacal silver nitrate was then added, the precipitate filtered off, washed, and decomposed on the filter paper with dilute hydrochloric acid. The filtrate from the silver chloride contains the histidine as hydrochloride, and on concentration to a small volume the histidine crystallises out as the dihydrochloride in characteristic glassy plates or prisms. The crystals formed are well developed, even when but a small quantity of histidine is present, and can easily be separated and purified by re-crystallising from dilute hydrochloric acid. The crystals are quite characteristic, and a crystallographic description has been given by Schwantke (*Zeit. Phys. Chem.*, 1900, xxix., 491) and Kossel (*Zeit. Phys. Chem.*, 1896, xxii., 182).

The characteristic form of the crystals, and the method by which the compound was obtained, are sufficient to establish its identity as histidine dihydrochloride, and can be confirmed by two colour reactions. Knoop's colour reaction: To a solution of the histidine salt add bromine water until the yellow colour produced is permanent. On heating the colour disappears, but is replaced shortly by a faint red, which gradually passes to a deep red, amorphous particles separating, and the liquid becoming turbid. This reaction is not very delicate, and is interfered with by the presence of free alkali or excess of bromine. Pauly's diazo reaction (*Zeit. Phys. Chem.*, 1904, xlii., 508): Histidine, or its salts in alkaline solution, give with diazo-sulphanilic acid a red colour which does not disappear on dilution. Tyrosine also gives a similar colour, but histidine or its salts can not be confused with tyrosine in crystalline form, the latter crystallising in needles that are nearly insoluble in water. This reaction is much more delicate than the one with bromine—one part in 100,000 is said to give a distinct pink colour.

The histidine dihydrochloride obtained from the soil gave both these colour reactions, the latter very definitely.

The histidine dihydrochloride obtained by this method is easily soluble in water, crystallises without water of crystallisation, and melts at 231° C. with some charring below this point. The free base can be obtained from the dihydrochloride by decomposition with silver sulphate. It is not very soluble in water, and crystallises in plates or needles. It is faintly alkaline in reaction, but does not take up carbon dioxide.

#### *Arginine, C<sub>6</sub>H<sub>14</sub>O<sub>2</sub>N<sub>4</sub>.*

The method of isolating arginine, which was simply a further step in the method used in the isolation of histidine, was as follows:—The filtrate from the histidine silver precipitate was saturated with powdered barium hydroxide, the precipitate filtered off, washed with barium hydroxide solution, suspended in dilute sulphuric acid, and decomposed with hydrogen sulphide. The filtrate from the silver sulphide was freed from sulphuric acid with barium hydroxide, and the filtrate from excess of barium with carbon dioxide. The filtrate from the barium carbonate was neutralised with nitric acid and evaporated to a small volume when arginine nitrate crystallised out. The neutral nitrate, C<sub>6</sub>H<sub>14</sub>O<sub>2</sub>N<sub>4</sub>.HNO<sub>3</sub>.H<sub>2</sub>O, thus obtained crystallises from water in opaque masses composed of minute needles. When anhydrous it melts at about 175° C., but not sharply. It is easily soluble in water, easily in hot alcohol, but with difficulty in cold. An acid nitrate, C<sub>6</sub>H<sub>14</sub>O<sub>2</sub>N<sub>4</sub>.2HNO<sub>3</sub>, can be obtained by evaporating the neutral nitrate with excess of nitric acid. It crystallises without water of crystallisation in long needles or plates and melts at 145° C. The free base can be obtained by adding silver nitrate solution to the acid nitrate solution, and then treating this with sodium hydroxide solution, when arginine silver is precipitated. This is decomposed with hydrogen sulphide. The filtrate from the silver sulphide on concentration deposits the free base in rosette-like masses of plates melting at 207° C.

The arginine obtained from the soil as neutral nitrate

\* Bulletin No. 74, U.S. Department of Agriculture, Bureau of Soils.

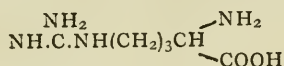
by the method described (Gulewitsch, *Zeit. Phys. Chem.*, 1899, xxvii., 189) was found to conform to the description of this salt, as did also the acid nitrate and free base made from it.

The method by which it was obtained and this conformity in crystalline form, melting-point, and other properties are sufficient to establish the identity of the compound obtained as arginine.

The quantity of arginine obtained from the Houston clay soil was much smaller than the quantity of histidine, and histidine has been obtained from several other soils from which no arginine could be obtained.

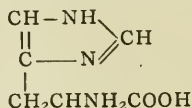
The isolation of histidine and arginine from soils has several points of theoretical interest. They are basic compounds capable of neutralising acids. The compounds resulting from the decomposition of organic matter are commonly thought of as essentially acid in character, and it is true that practically all that arise from carbohydrates are acid in character, as are also the majority arising from the decomposition of fats. However, the great majority of those derived from the decomposition of protein, while not actually basic as are arginine and histidine, are, when nitrogenous, potentially basic in that they contain the amino,  $\text{NH}_2$ , group. Even when the acid character predominates, as in monamino acids, they can unite with strong acids to form salts.

The constitution of both arginine and histidine is known. Arginine is guanidine  $\alpha$ -amino normal valerianic acid:—



(Schulze and Winterstein, *Zeit. Phys. Chem.*, 1898, xxvi., 1; Ellinger, *Zeit. Phys. Chem.*, 1900, xxix., 334; Kutscher, *Zeit. Phys. Chem.*, 1901, xxxii., 278, 413; 1904, xlii., 93; Fischer, *Ber.*, 1901, xxxiv., 454).

Histidine has the following constitution:—



(Pauly, *Zeit. Phys. Chem.*, 1904, xlii., 513; Knoop and Windaus, *Beit. Chem. Phys. Path.*, 1906, vii., 144; 1906, viii., 406; Knoop, *Ibid.*, 1907, x., 111).

Histidine is then an imidazole derivative, and contains but one amido  $\text{NH}_2$  group, and is not a diamino acid. It has, however, been so long classed with the diamino acids that it is included in that group here.

Both have, as have all amino acids derived from protein, an amino group in the  $\alpha$  position.

#### PYRIMIDINE DERIVATIVES.

Some of the pyrimidine bases, uracil, cytosine, and thymine, are constant products of the decomposition of the nucleic acid of nucleo-proteids, and while all three may be present as the result of the decomposition of nucleic acids of animal origin, thymine seems to be absent from those of plant origin.

The plant nucleic acids studied are as yet few in number. That of yeast is the best known, and has been extensively investigated by Kossel (*Zeit. Phys. Chem.*, 1879, iii., 284; 1880, iv., 290; 1882, vii., 7). Osborne and Harris (*Zeit. Phys. Chem.*, 1902, xxxvi., 85; *Journ. Am. Chem. Soc.*, 1900, xxii., 379) have isolated a nucleic acid from the wheat embryo which seems to be identical with yeast nucleic acid. Klinkenberg (*Zeit. Phys. Chem.*, 1882, vi., 155) obtained from palm cake and poppy seed nucleic acid resembling that of yeast in composition, and there is every reason to conclude that in plants, as in animals, all parts rich in cells are rich in nucleic acids.

In addition to the nucleic acids of higher plants, which may make up a portion of the organic matter of soils, the

micro-organisms which are so abundant in soils contain and probably elaborate nucleo-proteids from other nitrogenous material. Galeotti (*Zeit. Phys. Chem.*, 1898, xxv., 48) found nucleo-proteid in bacteria, and Stutzer (*Zeit. Phys. Chem.*, 1882, vi., 572) has shown that 40 per cent of the nitrogen of moulds is nuclein nitrogen.

There are, then, two ways in which nucleic acids and their decomposition products may become part of the soil: From the introduction of the nucleic acids of higher plants on the death and decay of the same in the soil; and from nucleo-proteids elaborated in the soil from other nitrogenous compounds by micro-organisms.

#### Cytosine, $\text{C}_4\text{H}_5\text{ON}_3\cdot\text{H}_2\text{O}$ .

A crystalline compound identified as the pyrimidine base, cytosine, has been isolated from several soils by the following method:—The soil was treated for several hours with 2 per cent sodium-hydroxide solution, allowed to stand, and the dark coloured extract syphoned off. This was acidified with dilute nitric acid and filtered from the humus precipitate. The acid filtrate was then neutralised with sodium hydroxide and filtered from the precipitate formed. The neutral filtrate was then treated with an excess of mercuric nitrate, and the whole brought to neutrality again with sodium hydroxide. The precipitate formed was filtered off, washed, and decomposed by hydrogen sulphide. The filtrate from the mercuric sulphide was concentrated to a small volume, and silver nitrate added in slight excess and filtered from the coloured precipitate formed. To the filtrate dilute ammonia was carefully added until a precipitate was no longer formed. An excess of ammonia was avoided since the precipitate is dissolved thereby. The silver precipitate was separated by filtration, washed, and suspended in hot water, and decomposed by hydrogen sulphide. The filtrate from the silver sulphide was concentrated to a small volume and allowed to stand, when crystals formed in a short time.

These crystals were in the form of needles or thin shining plates with uneven faces. The compound was purified by re-crystallising several times from water. Thus prepared, the compound is in the form of clear crystals, which on exposure to the air lose water and become opaque. It does not melt at  $300^\circ\text{C}$ ., but darkens slightly. It is difficultly soluble in cold water, but readily in hot, from which solution it rapidly separates on cooling. The relative solubility in hot and cold water is influenced by impurities which generally accompany the first crude separation. It is difficultly soluble in alcohol and insoluble in ether. The water solution is neutral in reaction, but compounds of definite crystalline appearance are formed with mineral acids. The sulphate crystallises in needles and the hydrochloride in prisms. Addition of sodium picrate to a water solution forms a difficultly soluble picrate, crystallising in needles. A difficultly soluble chloroplatinate is formed, crystallising in characteristic prisms. Addition of potassium bismuth iodide to an acidified water solution forms a red micro-crystalline precipitate.

These reactions, the crystalline appearance of the compound, and the method by which it was obtained establish its identity as cytosine. The identification was further confirmed by the following determinations:—A pure preparation crystallised from water, dried a short time between filter paper, lost water of crystallisation at  $100^\circ\text{C}$ .

|                            | Found. | Calculated for<br>$\text{C}_4\text{H}_5\text{N}_3\text{O}\cdot\text{H}_2\text{O}$ . |
|----------------------------|--------|-------------------------------------------------------------------------------------|
| Water of crystallisation.. | 13.79  | 13.97                                                                               |

It was found to contain nitrogen corresponding to the formula for cytosine:—

|                  | Found. | Calculated for<br>$\text{C}_4\text{H}_5\text{N}_3\text{O}$ . |
|------------------|--------|--------------------------------------------------------------|
| Nitrogen .. .. . | 37.92  | 37.84                                                        |

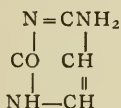
These figures are sufficient to make the identification certain.



A modification of the method by which cytosine was obtained that had some advantages is as follows:—Acidify the alkaline-soil extract with sulphuric acid, filter from the humus precipitate, and to the acid filtrate add a solution of mercuric sulphate in 5 per cent sulphuric acid, using an excess. Filter from any precipitate that may be formed immediately, and allow the filtrate to stand several days. The precipitate formed should contain the cytosine. This precipitate, after being filtered off and washed, is decomposed with hydrogen sulphide, and the filtrate treated with silver nitrate as in the method first described.

The cytosine can also be obtained from the neutral solution obtained, as in the first method, without the preliminary precipitation with mercuric nitrate by treating the neutral solution with silver nitrate in the manner described. In this case, however, the final solution contains histidine, if any is present in the soil. Histidine does not interfere with the crystallisation of the cytosine, but other unknown impurities, which the mercuric-nitrate precipitation removes, accompany the two.

Cytosine was discovered by Kossel and Neumann (*Ber.*, 1894, xxvii., 2215) among the products resulting from treating yeast nucleic acid with sulphuric acid. Its constitution was determined by Kossel and Steudel (*Zeit. Phys. Chem.*, 1902, xxxvii., 177, 377; 1903, xxxvii., 49), and it was made synthetically by Wheeler, Johnson, and Jamieson (*Am. Chem. Journ.*, 1903, xxix., 492; 1904, xxxii., 342). Its structure is represented by the formula—



The closely related compounds uracil,  $\text{C}_4\text{H}_4\text{O}_2\text{N}_2$ , and thymine,  $\text{C}_5\text{H}_6\text{O}_2\text{N}_2$ , as has been stated, are also obtained by the decomposition of nucleic acids. Cytosine, while obtained from nucleic acids of various origin, seems to take the place of thymine in those of vegetable origin, so far as they have been investigated. In addition to being obtained from yeast-nucleic acid, it has been obtained from the nucleic acid of the wheat embryo (Wheeler and Johnson, *Am. Chem. Journ.*, 1903, xxix., 505).

The nucleic acids are not split into the pyrimidine derivatives and other decomposition products by the proteolytic enzymes, such as pepsin and trypsin, but this cleavage can be brought about by erepsin and other closely related enzymes, which have been called nucleases (Nakayama, *Zeit. Phys. Chem.*, 1904, xli., 348; Iwanoff, *Ibid.*, 1903, xxxix., 31; Sachs, "Ist die Nuklease mit dem Trypsin identisch." Inaug. Dissert. Heidelberg, 1905). Micro-organisms also effect a similar decomposition (Schittenhelm and Schröter, *Zeit. Phys. Chem.*, 1904, xli., 284). From this it would seem that the decomposition products of nucleic acids should be of as constant occurrence in soils as nucleo-proteins are in plants.

The soil from which cytosine was isolated in the manner described was the Marshall loam, a soil that has been described in connection with the isolation of other compounds. Crystals similar in appearance and properties have been isolated by the same method for several other soils, and the indications are that pyrimidine derivatives are present as part of the organic matter of many soils.

(To be continued)

Isomerism of Corynanthine and Yohimbine.—E. Fourneau and M. Fiore.—The alkaloid of pseudocinchona (corynanthine) and yohimbine are isomers, having the formula  $\text{C}_{21}\text{H}_{26}\text{N}_2\text{O}_3$ . The former is laevorotatory, and the latter dextrorotatory. Quebrachine has also the same formula, and may be the optical isomer of corynanthine.—*Bull. Soc. Chim. de France*, ix.-x., No. 23.

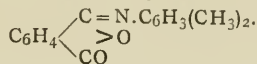
## ISOMERIC PHENYLPHTHALIMIDES AND SOME ALLIED COMPOUNDS.\*

### II.

By MITSURU KUHARA and SHIGERU KOMATSU.

(Continued from p. 44).

#### 6. *a*-as-Metaxylylphthalimide,—



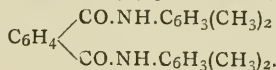
By the interaction of *as*-metaxylylidine and phthalyl chloride at  $-10^\circ$  in an ethereal solution, a yellow precipitate was produced. The precipitate was washed successively with ice cold hydrochloric acid, ammonia, and water; and then treated with ether, by which *a*-*as*-metaxylylphthalimide passed into solution. On evaporating ether, it crystallised in yellow needles, and its melting-point was found to be  $142-143^\circ$ . It is readily soluble in acetone, chloroform, benzene, ether, and alcohol. The substance was analysed and the results are as follows:—

- I. 0.2332 grm. of the substance gave 0.6506 grm.  $\text{CO}_2$  and 0.1185 grm.  $\text{H}_2\text{O}$ .
- II. 0.4373 grm. of the substance gave 21.4 cc. N ( $25.4^\circ$ , 754.5 mm.).
- III. 0.5693 grm. of the substance gave 28.8 cc. N ( $25.5^\circ$ , 752 mm.).

|             | Calculated for<br>$\text{C}=\text{N} \cdot \text{C}_6\text{H}_3(\text{CH}_3)_2$<br>$>\text{O}$<br>$\text{CO}$ | Found. |      |      |
|-------------|---------------------------------------------------------------------------------------------------------------|--------|------|------|
|             |                                                                                                               | I.     | II.  | III. |
| Carbon ..   | 76.50                                                                                                         | 76.07  | —    | —    |
| Hydrogen .. | 5.18                                                                                                          | 5.62   | —    | —    |
| Oxygen ..   | 12.78                                                                                                         | —      | —    | —    |
| Nitrogen .. | 5.58                                                                                                          | —      | 5.47 | 5.54 |

By the action of mineral acids or alkali, the substance is transposed to colourless metaxylylphthalimide with excessive readiness, which ought to possess the normal or symmetrical constitution.

#### 7. *Di*-*as*-metaxylylphthalimide,—



The insoluble portion in ether, obtained in the preparation of *a*-*as*-metaxylylphthalimide, was treated with hot alcohol to free it from the normal or *s*-*as*-metaxylylphthalimide simultaneously formed and mixed with it. The less soluble portion crystallised in silky needles from the large quantity of boiling alcohol. It gave, on analysis, the following results:—

- I. 0.2362 grm. of the substance gave 0.6737 grm.  $\text{CO}_2$  and 0.1435 grm.  $\text{H}_2\text{O}$ .
- II. 0.4705 grm. of the substance gave 30.7 cc. N ( $23.5^\circ$ , 757 mm.).
- III. 0.4141 grm. of the substance gave 27 cc. N. ( $24^\circ$ , 755 mm.).

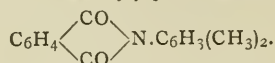
|             | Calculated for<br>$\text{C}_6\text{H}_4[\text{CONH} \cdot \text{C}_6\text{H}_3(\text{CH}_3)_2]_2$ | Found. |      |      |
|-------------|---------------------------------------------------------------------------------------------------|--------|------|------|
|             |                                                                                                   | I.     | II.  | III. |
| Carbon ..   | 77.42                                                                                             | 77.77  | —    | —    |
| Hydrogen .. | 6.45                                                                                              | 6.75   | —    | —    |
| Oxygen ..   | 8.10                                                                                              | —      | —    | —    |
| Nitrogen .. | 7.53                                                                                              | —      | 7.32 | 7.25 |

The substance is soluble in acetone, chloroform, and acetic acid, slightly in alcohol and benzene, but not in ether. It melts at  $202-203^\circ$ . It behaves like phenylphthalimide (*Memoirs of the College of Science, &c.*, i.,

\* *Memoirs of the College of Science and Engineering, Kyoto Imperial University*, ii., No. 12.

394) toward a dehydrating agent. By heating with phosphorus pentachloride, it yields a mixture of normal *as*-metaxylylphthalimide and di-*as*-metaxylylphthaldimide.

8. *s-as-Metaxylylphthalimide*,—

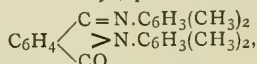


This substance was formed by the interaction of *as*-metaxylylidine and phthalyl chloride or phthalic anhydride, and crystallised in fine needles from the alcoholic solution. Its melting-point was found to be  $154^\circ$ . It is slightly soluble in ether and petroleum benzene, but readily in alcohol, acetone, benzene, chloroform, acetic acid, and carbon bisulphide. Its analysis gave the following results:—

- I. 0.1136 grm. of the substance gave 0.3178 grm.  $\text{CO}_2$ , and 0.0575 grm.  $\text{H}_2\text{O}$ .  
II. 0.56 grm. of the substance gave 29 cc. N ( $25.5^\circ$ , 753.8 mm.).

|                | Calculated for                                                                                                                                   |  | Found. |      |
|----------------|--------------------------------------------------------------------------------------------------------------------------------------------------|--|--------|------|
|                | $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{CO} \\ \diagdown \text{CO} \end{array} \text{N} \cdot \text{C}_6\text{H}_3(\text{CH}_3)_2.$ |  | I.     | II.  |
| Carbon .. ..   | 76.50                                                                                                                                            |  | 76.29  | —    |
| Hydrogen .. .. | 5.18                                                                                                                                             |  | 5.63   | —    |
| Oxygen .. ..   | 12.78                                                                                                                                            |  | —      | —    |
| Nitrogen .. .. | 5.58                                                                                                                                             |  | —      | 5.70 |

9. *Di-as-metaxylylphthaldimide*,—

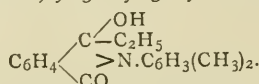


The mixture of this substance and *s-as*-metaxylylphthalimide was obtained by the action of phosphorus pentachloride upon di-*as*-metaxylylphthalimide in a dry chloroform solution, and two compounds were separated by fractional crystallisation from the alcoholic solution. The more soluble substance or di-*as*-metaxylylphthaldimide crystallises in yellow plates, and melts at  $149-150^\circ$ . It is soluble in ether, alcohol, benzene, and chloroform. The analysis of the substance gave the following results:—

- I. 0.1578 grm. of the substance gave 0.471 grm.  $\text{CO}_2$  and 0.0863 grm.  $\text{H}_2\text{O}$ .  
II. 0.1508 grm. of the substance gave 10 cc. N ( $16^\circ$ , 765 mm.).

|                | Calculated for                                                                                                                                                                                                     |  | Found. |      |
|----------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|--------|------|
|                | $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C} = \text{N} \cdot \text{C}_6\text{H}_3(\text{CH}_3)_2 \\ \diagdown > \text{N} \cdot \text{C}_6\text{H}_3(\text{CH}_3)_2 \\ \diagdown \text{CO} \end{array}$ |  | I.     | II.  |
| Carbon .. ..   | 81.35                                                                                                                                                                                                              |  | 81.37  | —    |
| Hydrogen .. .. | 6.22                                                                                                                                                                                                               |  | 6.10   | —    |
| Oxygen .. ..   | 4.52                                                                                                                                                                                                               |  | —      | —    |
| Nitrogen .. .. | 7.91                                                                                                                                                                                                               |  | —      | 7.75 |

10. *2-as-Metaxylyl-3-ethyl-3-oxy-isoinolinone*,—



This substance was prepared from both *a-as*-metaxylylphthalimide and *s-as*-metaxylylphthalimide by the action of magnesium ethyl iodide. It crystallises in colourless plates from the ethereal solution. It is soluble in ether and alcohol, and melts at  $176-177^\circ$ . Its analytical results are as follows:—

- I. 0.204 grm. of the substance gave 0.57 grm.  $\text{CO}_2$  and 0.133 grm.  $\text{H}_2\text{O}$ .  
II. 0.2218 grm. of the substance gave 9.4 cc. N ( $16^\circ$ , 62 mm.).

|                | Calculated for                                                                                                                                                                                                                                 |  | Found. |      |
|----------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--|--------|------|
|                | $\text{C}_6\text{H}_4 \begin{array}{c} \diagup \text{C} \begin{array}{c} \diagup \text{OH} \\ \diagdown \text{C}_2\text{H}_5 \end{array} \\ \diagdown > \text{N} \cdot \text{C}_6\text{H}_3(\text{CH}_3)_2 \\ \diagdown \text{CO} \end{array}$ |  | I.     | II.  |
| Carbon .. ..   | 76.87                                                                                                                                                                                                                                          |  | 76.22  | —    |
| Hydrogen .. .. | 6.76                                                                                                                                                                                                                                           |  | 7.22   | —    |
| Oxygen .. ..   | 11.39                                                                                                                                                                                                                                          |  | —      | —    |
| Nitrogen .. .. | 4.98                                                                                                                                                                                                                                           |  | —      | 4.94 |

(To be continued).

## ASSAY METHOD FOR TUNGSTEN.

By B. M. DIVANI.

WHEN tungsten is in solution in the condition of tungstate it is possible to precipitate and estimate the tungsten in the form of the trioxide  $\text{WO}_3$ . To effect this, all that is needed is to render the solution acidic by means of hydrochloric or nitric or even sulphuric acid.

Tungstic acid is soluble to some slight extent in mineral acids. On that account it is advised in the usual works on analytical chemistry to render the tungstic acid insoluble by repeated evaporation on a hot water-bath, the solution to which an excess of acid has been added, after which the dry residue is warmed for some length of time at a temperature of  $120^\circ \text{C}$ .

To avoid these operations, which are rather tedious and time-consuming, the writer recommends for study a method of determining tungsten based on the precipitation of tungstic acid by an excess of a solution of freshly prepared stannous chloride. The stannous chloride precipitates the tungsten from solution in the form of the tungsten oxide  $\text{W}_2\text{O}_5$ . It is well known that this reaction is quite sensitive.

In order to assure himself to what extent precipitation is complete, and also that the oxide be not reduced during washing, the following experiments were tried by the writer:—

Two grms. of absolutely pure tungstic acid was dissolved in just enough concentrated ammonia to dissolve that amount of acid, and the volume of this solution was brought up to 1 litre. Caustic soda or potash might have been chosen just as well, the choice of alkali having no effect on the precision of the operations.

For each test determination 50 cc. of this solution were taken, containing therefore 0.1 grm. of tungstic acid. To precipitate the tungsten oxide from this solution the author added 20 cc. of a solution of stannous chloride. The latter was so concentrated as to contain 50 grms. of crystal salts per 200 cc. of concentrated hydrochloric acid. After boiling the mixture for one or two minutes the precipitate was permitted to settle.

The precipitate was then washed in warm water. Since the oxide of tungsten is deposited very readily it is possible to wash the precipitate several times within a few minutes without having the water cool sufficiently to float the precipitate. Under these conditions the precipitate remains flocculent, and no cloudiness is produced in the water-bath. The oxide thus precipitated was calcined and weighed as the trioxide. The results indicated that this method was susceptible of an unusually high degree of accuracy.

In order to be sure that in the calcined residues measured in the above tests no tin was carried along, the following analyses were made:—Several of the residues were collected and heated in a current of hydrogen. The production was subjected to hydrochloric acid and filtered. A current of sulphuretted hydrogen gas was passed through the filtrate. This reaction gave no precipitate. Hence no tin was carried along in the precipitation of tungsten trioxide.

The author also tried some experiments, the aim of which was to ascertain whether the presence of iron affects the accuracy of the method. With this end in view there were added to a couple of tested samples 10 to 20 cc. of a solution of ferric chloride, half normal. The results showed that iron produces no effect on the accuracy of the method.—*The Chemical Engineer*, xiv., No. 4.



EIGHTH INTERNATIONAL CONGRESS OF  
APPLIED CHEMISTRY,  
WASHINGTON AND NEW YORK, SEPTEMBER, 1912.

*Rules on Papers, their Presentation, Discussion, and Publication.*

In order that the objects of the Congress may be attained, the following instructions to all prospective authors of contributions are necessary:—

- a. That as many as possible of the papers to be presented at the various meetings of the Congress, and its various Sections, be printed and distributed to members attending the Congress prior to the opening thereof.
- b. That as little time be given to presentation as is consistent with adequate exposition of the salient points of the communication.
- c. That as much time and opportunity be given for discussion as may be needed for a complete presentation of all the views of those members in attendance upon such discussion.
- d. That the discussions be recorded in sufficiently full manner correctly to reflect the views of those taking part in the discussion.
- e. That the Proceedings be published in complete form as soon after the close of the Congress as is at all feasible.

After considerable study, enquiry, and exhaustive criticism of the tentative rules submitted to the chemists and the chemical and similar societies of the world, March 6th, 1911, and September 1st, 1911, the Executive Committee of this Congress has concluded that hearty and earnest co-operation of all members of the Congress in the carrying out of the following rules will result in the practical realisation of all these things; without such individual co-operation, the officers of the Congress can do very little toward such realisation.

Duplicate copies of papers and their abstracts are *thoroughly essential* to quick and accurate printing. Authors should have all their contributions in final form (see Rule 21).

1. Papers or other like contributions should be *original*, and *not elsewhere read or published*. However, prior publication of Governmental researches, which publication is made in accordance with the law of such country, shall be exempt from the above restriction as to publication.

2. All papers or like contributions should be as *concise* as possible, and must contain the name and post-office address of the respective authors. Further, what number, if any, of reprints is desired (see Rules 8 and 10).

3. All papers should be in *duplicate* and legibly written, preferably typewritten. Formulæ should be carefully inserted by hand as simply as possible.

4. Each sheet should be as nearly 8 × 12 inches as convenient, and should be written on one side only, and *not* on both sides.

5. Each paper should be accompanied by an abstract thereof in *duplicate*. Formulæ should be carefully inserted by hand as simply as possible.

6. All references to other work should state carefully the sources of the citation, giving the exact reference to the original publication.

7. Illustrations, curves, and the like should be on separate smooth white sheets, and drawn and lettered with Indian ink clearly enough to bear a linear reduction to one-half or two-thirds, and when so reduced should not exceed the page size of the "Report," which will be about 4½ by 7 inches.

8. Authors of papers which are to be illustrated by lantern slides are urgently requested to state on their paper the size of slide used, so that suitable arrangements may be made. Failure to observe this may result in disappointment and delay (see Rule 2).

9. The Congress obligates itself to have its final Report and Proceedings, including subject and authors' index, completed and ready for distribution on or before December 31st, 1912. In case those Reports and Proceedings be not ready for distribution by that date, authors of all papers received and accepted *after* June 30th, 1912, may then publish in any journal or publication that they may elect. (*Note:* This refers only to the Report and Proceedings bound in paper. Members desiring cloth bound sets can obtain them at an advanced charge over the 5.00 dols. membership fee. Such advanced charge will be announced later, but will probably be 2.50 dols. Delivery of these cloth bound sets will be about ninety days later than of the paper bound sets.)

Authors of papers received *before* the close of June 30th, 1912, may publish those papers in any publication they may elect *after* the paper is read, or *after* the Congress has adjourned (see Rule 12).

10. Authors of papers accepted and printed in full or in abstract will receive, free of cost and all delivery charges, not to exceed fifty (50), reprints of each paper or abstract. Additional copies of reprints can be had upon payment of the prices for such copies, which prices will be announced later. The Congress cannot undertake to furnish reprints of papers if the order for such reprints is not attached to the paper or abstract when received by the American Committee (see Rule 2).

11. Papers and their abstracts, *both in duplicate*, must be in the hands of the American Committee not later than June 30th, 1912. All papers received *prior* to that time and accepted will be printed in their respective Sectional Volumes, and distributed to such of the attending members of the Congress as may desire them, at or before the opening of the Congress. Papers received *after* that time, if accepted, will be printed, but may appear in an appendix which may or may not be ready by the opening of the Congress. The Congress cannot then undertake to print them along with the papers of those sections to which they may be assigned, and which were received prior to June 30th, 1912.

12. No paper offered to and accepted by this Congress can be at any time published elsewhere without giving credit to this Congress for such article or publication. However, Governmental publication of papers contributed to the Congress are exempt from the above requirement as to giving credit to this Congress.

13. All authors, as a matter of course, agree not to publish their accepted papers in any other publication except as herein provided, and, further, they agree to abide by any final decision of the Congress with respect to such paper or papers, their presentation, discussion, or printing.

14. Rejections by Sectional Committees will not be final; their decisions will be reviewed by the Committee on Papers and Publications, but rejection by that Committee will be final.

15. Authors of finally rejected contributions will be notified in writing of such rejection immediately after it has been made, and, as far as the Congress is concerned, such final rejection is strictly secret and confidential. Rejected manuscripts are to be returned to their authors (see Rule 16).

16. The Congress will not publish a list of rejected papers nor state what papers have been rejected; directly after the closing of the Congress all records relating to rejected papers and like contributions will be destroyed; any and all proceedings as to rejected papers or like contributions, so far as the Congress is concerned, will be strictly secret and confidential.

17. Any paper which is of a pronounced polemical, advertising, or personal character may be thereby disqualified and for that reason alone rejected, regardless of whatever merit the paper may otherwise possess.

18. The Congress reserves the right to reject any paper or other contribution that may be offered to it.

19. The Congress reserves the right to print the full

paper only, or the abstract only, or the title only, in each case with the author's name and post-office address.

20. Authors are requested to state on the papers themselves their preferences for the sections in which they wish them to be read; the Congress will respect that request wherever practicable, but reserves the right to assign the paper to any other section that may be deemed more appropriate, and such disposition is final.

21. Authors will *not* receive printer's proofs of their papers or abstracts; nor will their papers or abstracts be revised after receipt by the American Committees; printing will be accurate to copy.

22. The time consumed in reading or presenting the substance of any paper by an author or his representative at a meeting of a Section must not exceed ten (10) minutes, except by special permission of the Sectional Executive Committee.

23. In the absence of an author or his representative the paper will be read by title only, and if there be any discussion it must be based upon the paper as printed, because neither the paper itself nor its abstract will be read; exceptions to this rule can be made only under regulations that may be adopted by each Sectional Executive Committee.

24. Discussions of a pronounced polemical, advertising, or personal character may be ruled out by the Chair on that ground alone, and not permitted to appear in the printed record; the ruling of the Chair in such matters is final and is not subject to revision or appeal.

25. Participants in discussions will be given an opportunity of editing the manuscript reports of their remarks, but printer's proofs will not necessarily be submitted to them, although wherever practicable they will be so supplied.

26. Participants in discussions must speak from the rostrum and *not* from the floor.

Respectfully,

EDWARD W. MORLEY, Honorary President.  
WILLIAM H. NICHOLS, President.  
BERNHARD C. HESSE, Secretary.

28, Broad Street, New York City,  
December 28, 1911.

## PROCEEDINGS OF SOCIETIES.

### INSTITUTE OF CHEMISTRY.

#### "Cellulose."

At a Meeting of the Institute of Chemistry held at University College, London, on Friday, January 26th, Sir William Ramsay, K.C.B., presiding, a Lecture was delivered by Mr. CHARLES F. CROSS, B.Sc., F.I.C., on "Cellulose."

He said that in the text-books of chemical science "cellulose" takes an inconspicuous place; in other words, the labours of specialists in this field have not contributed much to rank as systematic science. The advance, however, in the classification of a wide field of natural products and phenomena has resulted in formulating constitutional problems of necessarily great moment, and this is a contribution of "capital," if not, as yet, of "income."

Cellulose as a basis of manufacture takes by contrast a predominating position. Primary manufactured products at factory cost represent values approaching £200,000,000 per annum for the United Kingdom. Cellulose derivatives as the basis of smokeless powders, as an indispensable auxiliary to photographic art, and as the raw material of "celluloid," occupies various positions of unique and critical importance.

England more than maintains its competitive position in this huge field of industrial activity. Chemists are disposed to be pessimistic in contrasting the relative advance of Germany in chemical industry. But in the general perspective, the figures for gross production, as for the very special section of dye-stuffs and organic synthetic products, are insignificant. Taking cellulose as a typical colloid, and enlarging our view to include industries based upon colloids, *e.g.*, silk, wool, leather, gelatin, starch, paints and varnishes, indiarubber, &c., their preponderance is evident. In other words, excluding the metals, human industry is chiefly busy in transforming colloidal substances of entirely natural origin. Hence, a second feature of cellulose chemistry of great importance to the rising generation.

The normal cellulose is still rather a laboratory term and product, but of as obvious importance for cellulose industry as a gold standard for commerce. The lecturer insisted on its recognition, and demonstrated that the so-called "pure" cellulose in the form of chemical filter-papers represented about 90 to 95 per cent only of "normal" purity.

A normal cellulose is of the utmost importance in the explosives industry, and the supposed identity of "rag cellulose" (cotton and linen) with "normal cellulose" is an illusion.

"Lignocellulose," or wood substance, connotes a field of work of extraordinary attractiveness both scientific and industrial. After propounding a schematic constitutional formula for "lignone," and applying it to interpret characteristic reactions, the lecturer suggested that the type of combination of lignone with cellulose to form the complex "ligno-cellulose" may in time modify our views of chemical combination. The interpenetration of two colloidal systems may produce the effects of combination by "residues."

Attention was then directed to the industrial preparation of wood pulps and their typical forms:—"Soda" pulp, "sulphate" pulp, and "sulphite" pulp. These processes being taken as illustrating the balance sheet of industrial production, as establishing factory costs, and as an extension of the chemist's habitual methods of quantitative analysis.

As a special case, the interaction of chlorine and ligno-cellulose was considered as a potential industrial process that is of probable future value by reason of the new chlorine-soda equilibrium of the alkali world.

The lecture was illustrated by various specimens of special cellulose manufactures, artificial silks, "lustracelluloses," film products, transparent "pure" cellulose film—*not* celluloid—in lengths of 100 metres  $\times$  1 metre width, variously coloured and decorated; solid agglomerates (viscoid); and products from cellulose acetate in various forms.

The second lecture will be given on February 23rd.

National Insurance Act, 1911, Advisory Council.—The National Insurance Advisory Council, of No. 3, Northampton Square, London, E.C., is prepared to advise enquirers, whether employers or employed, male or female, who are desirous of ascertaining their position under the National Insurance Act. Special attention will be given to enquiries from registered friendly societies of less than 500 members, and unregistered societies, slate clubs, and yearly clubs, &c., as to the best manner in which to become approved. Arrangements can be made for speakers to be sent if desired. Any person desirous of making an enquiry, whether on his own behalf or on the behalf of any other person of either sex, or any society or club, should forward a letter containing full particulars and a stamped addressed envelope for reply to the Secretary at the above address. No charge will be made for any information given in response to any enquiry.



## NOTICES OF BOOKS.

*Collective Index of the Journal of the Institute of Brewing.*  
Compiled by WILLIAM H. BIRD, A.C.I.S. London:  
Harrison and Sons. 1911. (10s. 6d.).

THIS very complete index of the *Journal of the Institute of Brewing* is a volume which no brewer's chemist can afford to be without. It is divided into four parts. In the first the names of authors are given in alphabetical order, with the titles of the articles they have contributed. The second part is a subject list arranged alphabetically under the most important headings. A short list of general matter, including accounts of annual and other general meetings, annual reports, balance sheets, &c., form Part III., and the fourth part contains a list of journals from which abstracts have been taken. The index, which has been compiled by the Assistant Secretary to the Institute of Brewing, covers the years 1887-1911.

*Kurzes Lehrbuch der Organischen Chemie.* ("Short Text-book of Organic Chemistry"). By Prof. Dr. A. BERNTHSEN. Eleventh Edition, revised in collaboration with Dr. AUGUST DARAPSKY. Braunschweig: Friedr. Vieweg und Sohn. 1911. (12 Mk.).

THE eleventh edition of Bernthsen's excellent short text-book of organic chemistry contains considerably more matter than its predecessors, although the fact that it is printed on thinner paper makes it appear smaller. It retains the form and arrangement of the original, and will no doubt maintain its high reputation as a scholarly and comprehensive work on general organic chemistry. The chief alterations from the tenth edition lie in the addition of such new results of importance as have been reached since its issue; for example, a *résumé* is given of the work of Staudinger and others on ketones. Moreover, the application of the methods and results of physical chemistry to organic chemistry is treated in fuller detail, and sections have been added on, among other subjects, velocity of reaction and catalysis, electrolytic dissociation, and equilibrium reactions.

*Theorie und Praxis der Massanalyse.* ("Theory and Practice of Volumetric Analysis"). By ALEXANDER CLASSEN. Leipzig: Akademische Verlagsgesellschaft. 1912.

THIS comprehensive treatise on volumetric analysis will be a welcome addition to the chemist's library. In it every volumetric method used in pure chemistry is described in full detail, and all the necessary tables are included. The principles involved are also fully explained, with examples of the methods of calculating results. The theory of the subject is very carefully treated, and the special apparatus employed is illustrated. As a reference book on volumetric analysis containing the methods of determining volumetrically the rarer as well as the commoner elements it is difficult to see how it could be improved upon.

## CORRESPONDENCE.

### ON SCIENCE AND SILENCE.

To the Editor of the *Chemical News*.

SIR,—Will you kindly allow me the courtesy of your columns to air a grievance, which is, to some extent, personal, but which, nevertheless, is liable to become much more than personal, unless it is noted and remedied. I can best indicate its nature by quoting a passage from an article of mine on the "Dissipation of Energy," in the current number of the *Oxford and Cambridge Review*.

"Nevertheless, universal decay and silence has been, and still is, widely and dogmatically asserted by many

prominent men of science. In the standard text-books it is put forward, *ex cathedra*, with little attempt at reasoned defence or exposition. It is a dogma to be believed on pain of heresy. And heresy is met with that most potent form of scientific excommunication, silence. Those who deny current dogmas find a place in the new scientific index, where the heretics are labelled cranks. Thus there are dangers in our path when we make our investigations and endeavour to discover where the ultimate decay of the Universe is to be found."

May I say a few words as to the course of events which has inspired the above passage? Some time ago I wrote a thesis, which, among other things, asserted that all the current methods of estimating geologic time (with the possible exception of the radioactive method) were absolutely and fundamentally mistaken. Somewhat of a large order, the reader will say. Just so, but let him read a little further. The remarkable vicissitudes of that thesis it would take too long to describe. But, after much correspondence (heated and otherwise), worry and trouble, I succeeded in inducing a number of journals, particularly the *CHEMICAL NEWS*, the *Journal of Philosophy*, the *Journal of Geology*, *Knowledge* (under the old management), and the *New Quarterly* (now defunct) each to publish a snippet. The scientific journals were invariably too full to publish the section relating to Prof. Sollas' method based on the thickness of the sedimentary rocks. That, however, at last, by means of a personal introduction to the late Sir Percy Bunting, found a place, with some other matter, in the form of a popular article in the *Contemporary Review* (February, 1911). In every case, perhaps somewhat unwisely, steps have been taken to inform those criticised of the appearance of the articles. The consequence has been a number of letters from prominent men of science informing me *privately*, in effect, that I am right and that the experts are wrong. No criticism of any value has been elicited. But, so far as I am aware, the geologists and physicists have, so far as their public utterances are concerned, absolutely ignored the whole matter. It would appear as if it were of no importance whether or no there is any truth in current ideas on the most fundamental question of geology.

Now will you permit me to call attention to the article in question? In that article cogent reasons are given for the opinion that the one essay in cosmology of the science of the past century, viz., the doctrine of Clausius and Lord Kelvin, technically known as the Dissipation of Energy, is nothing but a transparent and gigantic fallacy, a fallacy which arose because, unfortunately, those prominent men of science were not also philosophers. The fallacy is traced to its source, and it is shown how the standard text-books copy without examination the errors of the great masters of science. Surely all this calls for a reply. There has not yet been time for a public controversy, but I write this letter so that the tactics by which men of science attempt to crush out those who dispute their views may not be repeated.

Once again, I have received expressions of opinion—*privately*. One of the greatest men of science of the day "likes it very much"; "I state my case very fairly." Another F.R.S. sent me *privately* a letter containing some helpful criticisms, but little encouragement. Verbally he was good enough to say that he thought its truth would be recognised in *fifty years' time*. Now I venture to submit that the matter is of importance. If there are errors it is as well to acknowledge and correct them. I can assure men of science that criticisms have not been written from a desire to find fault, or to set myself up as cleverer than other people. It is important that it should be known whether the statements I make are right or wrong. The matter affects the progress of philosophy. If I find that the correctness of my views is admitted by men of science publicly, I shall base certain philosophical doctrines on that fact. I shall infer that the mistakes have been made for such and such reasons. If, on the other hand, I am wrong, I must modify my subsequent work accordingly.

May I make an appeal to men of science, particularly those like Prof. J. J. Thomson and Prof. Poynting, whose text-book is attacked, to break the monotony by saying something. It is so easy to flatter in private and ignore in public. It is so easy to refuse publication in the recognised journals, to refuse to notice the articles when they do appear, to say nothing, and then, when the author is dead, or has turned to other topics, to dig up the ideas, distribute them, publish them under other names, and pretend not to know where the ideas come from. It is easy, but does it not show that the race of men of science is degenerating? Would Huxley, or even Kelvin himself, who, at least, was great enough to acknowledge a mistake, have connived at tactics of this kind.

I am indebted to you, Sir, for promising to publish this letter, but it will say more for the honour of the men of science when such a letter cannot be written.—I am, &c.,

H. S. SHELTON.

Ashford, Middlesex, January 23rd, 1912.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. cliii., No. 25, December 18, 1911.

This number contains no chemical matter.

*Berichte der Deutschen Chemischen Gesellschaft.*  
Vol. xlv., No. 18, 1911.

Distinction between True Peroxy-salts and Salts with  $H_2O_2$  of Crystallisation.—E. H. Riesenfeld and W. Mau.—A common property of all true peroxy-salts is the power of liberating iodine quantitatively from neutral potassium iodine solution, and of being gradually transformed into  $H_2O_2$ -addition products. This property enables the true peroxy-salts to be distinguished from the  $H_2O_2$ -addition products. Since true peroxy-salts in aqueous solution are spontaneously (*i.e.*, with liberation of energy) converted into  $H_2O_2$ -addition products they cannot be prepared in aqueous solution without the addition of energy.

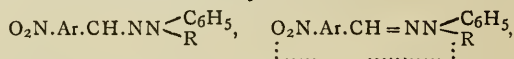
Isomeric Percarbonates.—E. H. Riesenfeld and W. Mau.—Carbonates containing peroxide oxygen may be grouped in three classes:—(i.) Carbonates with  $H_2O_2$  of crystallisation, *e.g.*,  $Na_2CO_3 \cdot 1\frac{1}{2}H_2O_2$ . (ii.) Mono-peroxy-carbonates, *e.g.*,  $Na_2CO_4$ . (iii.) Percarbonates (mono-peroxy-dicarbonates), *e.g.*,  $Na_2C_2O_6$ . The salts of the first and second series are isomeric, exhibiting co-ordination isomerism. The salts  $Na_2CO_3 \cdot H_2O_2 \cdot \frac{1}{2}H_2O$  and  $Na_2CO_3 \cdot 1\frac{1}{2}H_2O$  have the same stoichiometric composition, but differ in chemical behaviour; thus the former separates no iodine from a neutral potassium iodide solution, while the latter sets free an amount which corresponds to about a third of its active oxygen. Percarbonates exhibit a different kind of isomerism. When prepared electrolytically they separate iodine almost quantitatively from potassium iodide solution, but when they are prepared by the action of carbon dioxide on alkali peroxide only about one-third of the iodine is set free. The percarbonates obtained by electrolysis appear to be analogous to the salts of persulphuric acid, while those obtained from carbon dioxide and alkali peroxide resemble the salts of sulphoperoxy acid.

*Atti della Reale Accademia dei Lincei.*  
Vol. xx., No. 10, 1911.

Formation of Solid Solutions by Halogen Salts of Potassium.—M. Amadori and G. Pampanini.—KCl and KBr are miscible in all proportions at both high and low temperatures. The miscibility of KBr and KI is limited at low temperatures (0.24 mol. per cent KBr in KI;

0.7 mol. per cent KI in KBr). At high temperatures their miscibility is complete. KCl and KI are miscible to a limited extent at low temperatures (0.7 mol. per cent KCl in KI; 0.1 mol. per cent KI in KCl). At high temperatures the miscibility is greater, but not complete (0.49 mol. per cent KCl in KI; 0.9 mol. per cent KI in KCl). Since the miscibility in the solid state is a measure of the degree of isomorphism it may be deduced that KCl and KBr are perfectly isomorphous, and that KBr and KI are isomorphous at high temperatures.

Nitroderivatives and Nitrohydrazones.—R. Ciusa.—In general the hydrazones of aromatic nitroaldehydes exist in yellow, red, and orange forms, and the difference in colour cannot always be attributed to the different positions of the nitric group. According to the author's view a nitrohydrazone of formula  $O_2N \cdot Ar \cdot CH : NN \cdot C_6H_5$  can give two chromoisomers, for it may or may not give rise to an internal addition product thus:—



The red compound appears to possess the maleic and the yellow the fumaric form.

Thermic Analysis of Binary Mixtures of Chlorides of Monovalent Elements.—C. Sandonnini and P. C. Aureggi.—Rubidium chloride gives a single eutectic with silver chloride. Thallium chloride gives one eutectic with lithium chloride and one with sodium chloride; with potassium and rubidium chlorides it gives mixed crystals in many proportions; with silver chloride thallium chloride gives a compound of composition  $2AgCl \cdot 3TlCl$ . Experiments with the system  $RbCl-CuCl$  reveal the existence of two compounds,  $2RbCl \cdot CuCl$  and  $2RbCl \cdot 3CuCl$ , while potassium chloride gives only the compound  $2KCl \cdot CuCl$ .

## MEETINGS FOR THE WEEK.

- MONDAY, 5th.—Royal Society of Arts, 8. (Cantor Lecture). "The Meat Industry," by Loudon M. Douglas, F.R.S.E.  
— Royal Institution, 5. General Monthly Meeting.  
— Society of Chemical Industry, 8. Discussion on "The Industrial Bursaries Scheme of the Commissioners of the 1851 Exhibition." "Constant Temperature Heating Apparatus for Explosives" and "Experiments on the Decomposition of Nitro-cellulose," by J. S. S. Brame. "Some Physical Constants of Structureless Cellulose Filaments (Artificial Silk)," by W. P. Dreaper and J. G. Davis.
- TUESDAY, 6th.—Royal Institution, 3. "The Study of Genetics," by Prof. W. Bateson, F.R.S.  
— Royal Society of Arts, 4.30. "Irrigation in South Africa," by W. A. Legg, M.Inst.C.E.
- WEDNESDAY, 7th.—Society of Public Analysts, 8. (Annual General Meeting). "Determination of Butter-fat and Coconut Oil in Margarine," by F. W. F. Arnaud and H. Hawley. "Souring of Milk," by H. D. Richmond and H. C. Huish. "A Flour Improver," by E. Hinks.  
— Royal Society of Arts, 8. "The Influence of Ozone in Ventilation," by Leonard Hill, M.B., F.R.S., and Martin Flack, M.A., M.B., B.Ch.
- THURSDAY, 8th.—Royal Institution, 3. "Phenomena of Splashes," by A. M. Worthington.  
— Royal Society of Arts, 4.30. "The North-East Frontier of India," by Col. Sir Thomas H. Holditch, R.E., K.C.M.G., &c.  
— Royal Society. "Spectrum of Comet Brooks (1911 C)," by Sir N. Lockyer. "Chemically Active Modification of Nitrogen produced by the Electric Discharge," by Hon. R. J. Strutt. "The Atomic Weight of Radium," by R. Whytlaw-Gray and Sir W. Ramsay. "Optical Determination of the Variation of Stress in a Thin Rectangular Plate subjected to Shear," by E. G. Coker. "Spectroscopic Observations—Lithium and Cesium," by P. V. Bevan. "Observation by means of a String Electrometer of Fluctuations in the Ionisation produced by  $\gamma$ -Rays," by T. H. Laby and P. W. Burbidge.
- FRIDAY, 9th.—Royal Institution, 9. "Very High Temperatures," by Dr. J. A. Harker, F.R.S.
- SATURDAY, 10th.—Royal Institution, 3. "Franz Liszt (Centenary)," by Sir Alexander C. Mackenzie, Mus. Doc., &c.



# THE CHEMICAL NEWS.

VOL. CV., No. 2724.

## CHEMICAL NATURE OF SOIL ORGANIC MATTER.\*

By OSWALD SCHREINER and EDMUND C. SHOREY.

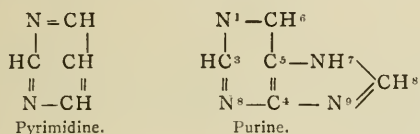
(Continued from p. 55).

### PURINE BASES.

THE purine bases, xanthine, hypoxanthine, adenine, and guanine, occur as such both in plant and animal tissues, but so far as known are always derived from the breaking down of nucleo-proteids. Three other purine bases, caffeine, theobromine, and theophylline, are the physiologically active principles in tea, coffee, and a number of other plants used as stimulants.

The purine bases are all derivatives of a body, purine,  $C_5H_4N_4$ , which has not been found in nature. The constitution of these bases is known, and they have been made synthetically (Fischer, *Ber.*, 1899, xxxii., 435).

As has been noted, purine is closely related to pyrimidine, and this relationship may be expressed by saying that purine contains a pyrimidine remainder. This relation is shown by the structural formulæ:—



The constitution of the four purine bases mentioned, and their relation to purine and each other, is expressed as follows:—

Xanthine is 2, 6. oxypurine;  
Hypoxanthine is 6. oxypurine;  
Adenine is 6. aminopurine;  
Guanine is 2. amino 6. oxypurine;

and they are also related to uric acid, which is 2.6.8. tri-oxypurine.

The purine bases are susceptible to the action of certain enzymes and of micro-organisms. It was shown by Schittenhelm and Schröter (*Zeit. Phys. Chem.*, 1903, xxxix., 203) that putrefactive bacteria, especially the *coli-bacillus*, were able to convert one purine base into another. In the animal organism it has been shown by Burian (*Zeit. Phys. Chem.*, 1905, xliii., 497) that xanthine and hypoxanthine are oxidised to uric acid by an oxidising enzyme. Guanine and adenine cannot, however, be oxidised directly in this way, but must first be deaminised by enzymes of another character, being converted thereby to xanthine and hypoxanthine respectively (Jones and Austrian, *Zeit. Phys. Chem.*, 1906, xlviii., 110; *Journ. Biol. Chem.*, 1907, iii., 227).

The same transformation of guanine and adenine into xanthine and hypoxanthine has been observed by Schindler in putrefaction (*Zeit. Phys. Chem.*, 1889, xiii., 432).

On the other hand, Kutscher (*Zeit. Phys. Chem.*, 1901, xxxii., 66) found that in the sterile autodigestion of yeast xanthine and hypoxanthine soon disappeared, leaving only guanine and adenine.

It would seem, then, that the purine bases are very susceptible to change one to another through the activity of enzymes or micro-organisms. Since investigation has shown some of these bases in the majority of soils

examined for them, it may be that further investigation will establish some relation between the presence of some one of these bases, and the presence of some particular micro-organism or combination of biological factors.

Two members of this group, xanthine and hypoxanthine, have been isolated from soils.

### Xanthine, $C_5H_4O_2N_4$ .

From the Marshall loam, containing 6.9 per cent organic carbon and 0.55 per cent total nitrogen, xanthine has been obtained by the following method:—

An extract of the soil was made in the manner used in the isolation of a number of other compounds, treating with 2 per cent sodium hydroxide. The dark coloured extract, after allowing the soil to settle, was syphoned off, and the alkaline liquid treated according to the method of Balke for the estimation of purine bases (*Journ. Prakt. Chem.*, 1893, [2], xlvii., 537). Fehling's solution, 10 cc. to each litre, was added and the solution heated to boiling. A few drops of a dilute solution of hydroxylamine hydrochloride were then added, and this continued until the precipitate formed was red in colour. The precipitate was separated by filtration, washed, and suspended in a fairly large volume of water, brought to boiling, and treated while hot with hydrogen sulphide. The filtrate from the copper sulphide was then concentrated on the water-bath. As this solution became concentrated a film or pellicle of white microcrystalline material formed on the surface, and when the liquid was reduced to a small volume this was removed by filtration. The substance so obtained, after purification by re-solution in hot water and separation on cooling, was a white microcrystalline powder, little soluble in cold water, but easily soluble in aqueous alkalis. A small quantity evaporated with nitric acid left a yellow residue, that on addition of sodium hydroxide and heating became yellowish-red and finally purple, the well-known xanthine reaction.

On dissolving the substance in ammonia and adding ammoniacal silver nitrate, a gelatinous precipitate was formed. This was soluble in hot dilute nitric acid (sp. gr. 1.1), and on cooling this solution there was no separation except on very long standing. This behaviour with ammoniacal silver nitrate distinguishes xanthine from other members of the group, and is used as a means of separation when they occur together. The ammoniacal silver nitrate precipitate is treated with boiling nitric acid (sp. gr. 1.1), when the xanthine and hypoxanthine precipitates dissolve, leaving adenine and guanine. From the solution so obtained hypoxanthine silver nitrate separates immediately on cooling. The xanthine remains in solution, and separates only, if at all, after long standing.

The substance obtained from the soil formed crystallised compounds with hydrochloric and nitric acids, the latter having the characteristic crystalline appearance of xanthine nitrate. On adding acetic acid to a very dilute solution of the compound in ammonia, and allowing to stand several days, groups of thin rhombic plates were obtained, having the characteristic appearance of xanthine obtained under these conditions. The method of isolation and the reactions described fix the compound as a purine base, and identify it as xanthine.

Instead of treating the alkaline soil extract as described, xanthine or other purine bases can be separated with advantage, in some cases by treatment of the acid solution resulting from acidifying the alkaline extract and filtering off the humus precipitate. This solution, made acid preferably with sulphuric acid, is heated to boiling, solution of copper sulphate added, and then a small quantity of a saturated solution of sodium bisulphite. The precipitate formed is filtered off and treated in the same manner as was the precipitate obtained with Fehling's solution. The advantage of the use of copper sulphate and sodium bisulphite lies in the fact that they can be used in neutral, acid, or alkaline solution.

Xanthine was first found in a urinary calculus in 1817, and since then has been found to be widely distributed in

\* Bulletin No. 74, U.S. Department of Agriculture, Bureau of Soils.

the tissues of both plants and animals. It has been found present as such in yellow lupines, sprouts of malt, in sprouts of lupines, in vicia sativa, in curcubita, in phaseolus, and in tea leaves, and no doubt further investigation will disclose its presence in many other plants (Salomon, *Dubois Archiv*, 1881, pp. 166, 361; Salomon, *Bot. Fahr.*, 1880, [1], p. 290; Schulze, *Landw. Fahr.*, 1883, xii., 912; Schulze, *Landw. Versuch.*, 1895, xlv., 383; Menozzi, *Ber.*, 1888, xxi., Ref. 619; Baginsky, *Zeit. Phys. Chem.*, 1884, viii., 395; Kossel, *Zeit. Phys. Chem.*, 1889, xiii., 298).

Xanthine then may get into the soil by the death and decay of plants that contain it as such, but it is probable that the most constant source of this, as well as other purine bases, is in the decomposition of nucleic acid and of nucleo-proteids in the soil.

#### Hypoxanthine, $C_5H_4ON_4$ .

Hypoxanthine, another purine base, has been isolated from a number of soils by one of the methods outlined in discussing xanthine. The alkaline soil extract, made with 2 per cent sodium hydroxide, was made slightly acid with sulphuric acid and filtered from the humus precipitate. Copper sulphate solution was added to the acid filtrate, the solution brought to boiling, and a saturated solution of sodium bisulphite added. The precipitate was separated by filtration, washed, suspended in hot water, and decomposed with hydrogen sulphide. The purine bases separate from the filtrate on concentration. Hypoxanthine, if the only one present, separates only on concentration to a small volume, as it is somewhat soluble in water. Its solubility is much influenced by the presence of impurities which accompany it in this procedure, and statements regarding its solubility by different authorities are very conflicting.

The free base obtained in this way is usually a micro-crystalline powder. It forms a hydrochloride of characteristic crystalline appearance, prisms, usually in clusters. It is dissociated by solution in water into the free base and hydrochloric acid.

Hypoxanthine does not give the xanthine reaction with nitric acid and alkalis, but if evaporated with bromine water and nitric acid a residue is left which turns red on heating with alkalis. Like other purine bases, it forms a gelatinous precipitate when ammoniacal silver nitrate is added to an ammoniacal solution, and this is dissolved by boiling nitric acid (sp. gr. 1.1), and separates from this solution immediately on cooling in characteristic microscopic needles or plates.

The identity of the compound obtained from the soil was established as a purine base by the method of its separation and its identity as hypoxanthine, proved by the appearance and properties of the free base, the crystalline appearance of the hydrochloride, its behaviour with bromine water and caustic soda, and the characteristic crystalline appearance of the silver nitrate compound.

Hypoxanthine was discovered first in the spleen and muscles of the heart, and like xanthine has been found to be widely distributed in plants and animals. It has been found in the juice of potatoes, in the juice of sugar beets, and together with xanthine in most plants where that compound has been found (Schulze, *Landw. Versuch.*, 1883, xxviii., 111; *Landw. Fahr.*, 1883, xii., 912; Lippmann, *Ber.*, 1896, xxix., 2645).

(To be continued).

**Line Spectrum of Nitrogen in Geissler Tubes.**—C. Porlezza.—Using very pure nitrogen the author has measured its line spectrum in a Geissler tube, and gives in this paper a complete table of his results, which frequently differ slightly from those of Plücker. The measurements extend over the visible spectrum from the red to the green.—*Atti della Reale Accademia dei Lincei*, xx., No. 10.

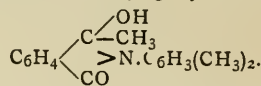
## ISOMERIC PHENYLPHTHALIMIDES AND SOME ALLIED COMPOUNDS.\*

### II.

By MITSURU KUHARA and SHIGERU KOMATSU.

(Continued from p. 56).

#### 11. 2-*as*-Metaxylyl-3-methyl-3-oxy-isorindolinone,—



THIS substance was obtained from both *a-as*-metaxylylphthalimide and *s-as*-metaxylylphthalimide by the action of magnesium methyl iodide. It is soluble in ether and alcohol. The crystals obtained from the ethereal solution melt at 161–162°. When crystallised from the alcoholic solution the substance contains alcohol of crystallisation. The crystals deposited from alcohol were carefully dried between folds of filter-paper, and heated in an air-bath at 80° for some hours. There was observed the loss of weight which must be due to the escape of the alcohol of crystallisation.

I. 0.534 grm. of the substance lost 0.075 grm. by weight on heating for two hours at 80°.

II. 0.7858 grm. of the substance lost 0.1113 grm. by weight on heating for three hours at 80°.

|             | Calculated for<br>$C_{17}H_{17}O_2N.C_2H_5OH$ . | Found. |       |
|-------------|-------------------------------------------------|--------|-------|
|             |                                                 | I.     | II.   |
| $C_2H_5.OH$ | .. 14.69                                        | 14.04  | 14.16 |

Again, the crystals dried at 80° were dissolved in methyl alcohol, and those deposited from that solution were heated at 70–80° for three hours, and the loss of weight was determined as the quantity of methyl alcohol of crystallisation.

0.6494 grm. of the substance lost 0.0668 grm. by weight on heating for three hours at 70–80°.

|           | Calc. for $C_{17}H_{17}O_2N.CH_3.OH$ . | Found. |
|-----------|----------------------------------------|--------|
| $CH_3.OH$ | .. 10.59                               | 10.16  |

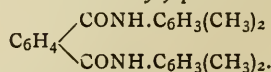
The substance which had lost the alcohol of crystallisation gave, on analysis, the following results:—

I. 0.1292 grm. of the substance gave 0.3627 grm.  $CO_2$ , and 0.077 grm.  $H_2O$ .

II. 0.1434 grm. of the substance gave 6.7 cc. N (14.5°, 758.6 mm.).

|          | Calculated for<br>$C_{17}H_{17}O_2N$ . | Found. |      |
|----------|----------------------------------------|--------|------|
|          |                                        | I.     | II.  |
| Carbon   | .. 76.41                               | 76.65  | —    |
| Hydrogen | .. 6.37                                | 6.62   | —    |
| Oxygen   | .. 11.99                               | —      | —    |
| Nitrogen | .. 5.29                                | —      | 5.47 |

#### 12. Di-*v*-orthoxylylphthalamide,—



The product of the interaction of *v*-orthoxylydine and phthalyl chloride, obtained by the method similar to that applied to metaxylydine and phthalyl chloride, was treated with ether, in which it was partly soluble. From the solution there were deposited yellow crystals which should be those of *a-v*-orthoxylylphthalimide, as the authors assume, but the analysis of the substance was impossible on account of its poor crop.

\* *Memoirs of the College of Science and Engineering, Kyoto Imperial University*, ii., No. 12.



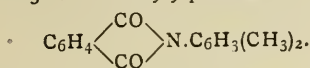
The insoluble portion, freed from *s-v*-orthoxylylphthalimide by treating with alcohol, was dissolved in boiling alcohol, and on allowing the solution to cool di-*v*-orthoxylylphthalimide crystallises in fine needles.

The substance melts at 192—193°. It is soluble in hot acetic acid and alcohol, but not in ether. Its analysis gave the results here recorded:—

- I. 0.2185 grm. of the substance gave 0.6245 grm. CO<sub>2</sub> and 0.1358 grm. H<sub>2</sub>O.  
II. 0.1584 grm. of the substance gave 10.4 cc. N (14°, 768 mm.).

|                | Calculated for<br>C <sub>6</sub> H <sub>4</sub><br>CONH.C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub> | Found. |      |
|----------------|-----------------------------------------------------------------------------------------------------------------------|--------|------|
|                |                                                                                                                       | I.     | II.  |
| Carbon .. ..   | 77.42                                                                                                                 | 77.94  | —    |
| Hydrogen .. .. | 6.45                                                                                                                  | 6.90   | —    |
| Oxygen .. ..   | 8.10                                                                                                                  | —      | —    |
| Nitrogen .. .. | 7.53                                                                                                                  | —      | 7.79 |

13. *s-v*-Orthoxylylphthalimide,—

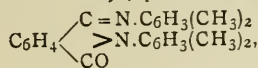


This substance was prepared by heating *v*-orthoxyldine and phthalic anhydride together or by the action of *v*-orthoxyldine upon phthalyl chloride. It crystallises in colourless needles from alcoholic solution, and melts at 143—144°. It is soluble in alcohol and benzene, but slightly in ether. Its analysis gave the following results:—

- I. 0.2236 grm. of the substance gave 0.622 grm. CO<sub>2</sub> and 0.1107 grm. H<sub>2</sub>O.  
II. 0.2144 grm. of the substance gave 10.1 cc. N (16°, 764 mm.).

|                | Calculated for<br>C <sub>6</sub> H <sub>4</sub><br>CO<br>CO<br>N.C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub> | Found. |      |
|----------------|--------------------------------------------------------------------------------------------------------------------------------|--------|------|
|                |                                                                                                                                | I.     | II.  |
| Carbon .. ..   | 76.10                                                                                                                          | 75.94  | —    |
| Hydrogen .. .. | 5.18                                                                                                                           | 5.50   | —    |
| Oxygen .. ..   | 13.14                                                                                                                          | —      | —    |
| Nitrogen .. .. | 5.58                                                                                                                           | —      | 5.50 |

14. Di-*v*-orthoxylylphthalidiimide,—

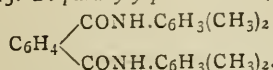


This compound was formed from di-*v*-orthoxylylphthalimide by the action of phosphorus pentachloride, as in the previous cases. It crystallises in yellow plates from alcohol, and melts at 123—124°. The analysis of the substance gave the results recorded below:—

- I. 0.2 grm. of the substance gave 0.595 grm. CO<sub>2</sub> and 0.1166 grm. H<sub>2</sub>O.  
II. 0.115 grm. of the substance gave 7 cc. N (12°, 755 mm.).

|                | Calculated for<br>C <sub>6</sub> H <sub>4</sub><br>C=N.C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub><br>CO<br>N.C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub> | Found. |      |
|----------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------|------|
|                |                                                                                                                                                                                               | I.     | II.  |
| Carbon .. ..   | 81.35                                                                                                                                                                                         | 81.14  | —    |
| Hydrogen .. .. | 6.22                                                                                                                                                                                          | 6.48   | —    |
| Oxygen .. ..   | 4.52                                                                                                                                                                                          | —      | —    |
| Nitrogen .. .. | 7.91                                                                                                                                                                                          | —      | 7.16 |

15. Di-*paraxylyl*phthalimide,—



By the action of paraxyldine upon phthalyl chloride in the ethereal solutions at low temperature, three substances were produced simultaneously; that is, di-*paraxylyl*phthal-

imide, *s-paraxylyl*phthalimide, and isomeric *a-paraxylyl*phthalimide. The last substance crystallises in amber coloured needles, and melts at 179—181°; but we were not able to get a quantity sufficient for analysis owing to its unstable nature, readily changing to *s-paraxylyl*phthalimide. The first of those substances or di-*paraxylyl*phthalimide crystallises in silky needles from hot alcoholic solution, and melts at 209—210°. It is soluble in hot alcohol, benzene, and chloroform, but not in ether. Its analysis gave the following results:—

- I. 0.1528 grm. of the substance gave 0.4347 grm. CO<sub>2</sub> and 0.0941 grm. H<sub>2</sub>O.  
II. 0.1652 grm. of the substance gave 10.6 cc. N. (16°, 764 mm.).

|                | Calculated for<br>C <sub>6</sub> H <sub>4</sub> [CONH.C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub> ] | Found. |      |
|----------------|-----------------------------------------------------------------------------------------------------------------------|--------|------|
|                |                                                                                                                       | I.     | II.  |
| Carbon .. ..   | 77.42                                                                                                                 | 77.62  | —    |
| Hydrogen .. .. | 6.45                                                                                                                  | 6.82   | —    |
| Oxygen .. ..   | 8.10                                                                                                                  | —      | —    |
| Nitrogen .. .. | 7.53                                                                                                                  | —      | 7.51 |

(To be continued).

## THE USE OF SULPHUR MONOCHLORIDE IN THE DETERMINATION AND ANALYSIS OF THE RARE EARTH MINERALS.\*

By WILLIAM BROOKS HICKS.†

MANY of the rare earth minerals contain columbium, tantalum, and titanium as their acid components. The usual methods of decomposing such minerals are fusion with potassium bisulphate, bifluoride, or by treatment with hydrofluoric acid. Each of these methods present difficulties. Fusion with potassium bisulphate is most generally used, but even when one fusion is sufficient to effect the decomposition, the resulting mixture containing all the earths is difficult to handle, particularly when a quantitative separation of the metallic acids from the other constituents is desired. On the other hand, the fluoride methods lend themselves to cleaner and more rapid separations, but are objectionable because they preclude the use of glass vessels. The present investigation introduces sulphur monochloride as a decomposing agent of such minerals, and it is applied in their analysis. Smith (*Journ. Am. Chem. Soc.*, 1898, xxii., 289), who was the first one to use sulphur monochloride in the decomposition of minerals, showed that many naturally occurring sulphides, as well as rutile, wolframite, scheelite, and columbite, were decomposed by this reagent. Oddo and Serra, two Italian chemists (*Gaz. Chim. Ital.*, 1899, [2], xxix., 355), used it in the preparation of anhydrous chlorides of arsenic, antimony, and bismuth, while Hall applied it to the preparation of pentachloride of columbium (*Journ. Am. Chem. Soc.*, 1904, xxvi., 1243). He also observed that it decomposed such minerals as chromite and columbite, and that it converted many oxides into their corresponding chlorides, the notable exceptions being the oxides of boron and silicon. Bourion (*Ann. Chim. Phys.*, 1910, xx., 547) has used sulphur monochloride in the preparation of anhydrous chlorides in general, as well as for the decomposition and analysis of scheelite and wolframite. It, therefore, seemed probable to me that this reagent might decompose such minerals as fergusonite, eschynite, &c., with the formation of chlorides. Accordingly they were submitted to its action and the extent of their decomposition carefully noted. The rare earths, after the expulsion of the metallic acids, were examined for scandium. This method of decomposition was also used in the analysis of eschynite. At the outstart

\* From the *Journal of the American Chemical Society*, xxxiii., No. 9.

† Details may be found in the author's Inaugural Thesis, University of Pennsylvania, 1911.

samples of these minerals not altogether pure were used, and while the decomposition was apparently complete, it was felt necessary to submit only the purest material, free from all contamination, to the action of the vapours of sulphur monochloride. The result was that fergusonite was completely decomposed—not a trace of the metallic acids remained in the boat, and rare earths could not be detected in the volatile portion. Eschynite was readily and completely decomposed, and euxenite yielded without the slightest difficulty to the action of the decomposing agent. A picked sample of samarskite (0.6197 grm.) left a residue of 0.0078 grm., which meant a decomposition of 98.78 per cent. All of these minerals, in amounts varying from  $\frac{1}{2}$  to 25 grms., were placed in porcelain boats in a combustion tube, which was heated on a furnace while the vapours of sulphur monochloride were passed over them. As previously stated, the volatile chlorides of the metallic acids passed into the receiver, while the non-volatile chlorides or oxychlorides of the earth metals remained in the boat.

It was in these non-volatile portions of the minerals that search was made for scandium. In the case of fergusonite 50 grms. of the mineral were decomposed. The boat contents were then dissolved in water and filtered from the gang. Nitric acid was added to the filtrate and the solution evaporated to dryness. The residue was taken up in 800 cc. of 1:1 hydrochloric acid, and to this boiling solution were added gradually 15 grms. of sodium silicofluoride (Meyer, *Zeit. Anorg. Chem.*, 1908, lx., 154). The boiling was continued for half an hour, when a slowly subsiding and slightly coloured precipitate appeared. This was filtered and washed by boiling it with dilute hydrochloric acid. It was then converted into sulphate, and the solution treated while boiling with ammonium hydroxide. The resulting precipitate was dissolved in hydrochloric acid, and the excess of acid removed by evaporation. The concentrated neutral chloride solution was next added to 50 cc. of a 20 per cent sodium carbonate solution. The white precipitate which appeared at once readily dissolved, and on boiling the liquid for half an hour there was no trace of precipitation. This would indicate the absence of scandium. The treatment was repeated several times with different samples of the material with the same negative results for scandium. The substance which had been precipitated from a strongly acid solution with sodium silicofluoride, and which failed to give a precipitate on boiling with a 20 per cent sodium carbonate solution, was studied further. For example, it yielded a white precipitate with oxalic acid, even in strongly acid solutions. It was completely precipitated by sodium thiosulphate from neutral solution, and it showed an atomic weight of 224 on ignition of its sulphate to oxide. Further, it was found to be radioactive. These behaviours were taken as conclusive evidence that the substance under examination was thorium, which is not generally mentioned as a constituent of fergusonite, where it evidently exists to the amount of between 2 and 3 per cent.

When the residual chlorides from eschynite were taken up in 1:1 hydrochloric acid, and the solution treated with an excess of sodium silicofluoride at the boiling temperature, a copious precipitate appeared. It was washed with dilute hydrochloric acid, converted into the sulphate, and then back into the chloride. The latter when treated with sodium carbonate yielded a white precipitate after a few minutes' boiling. This precipitate was filtered, washed several times with a sodium carbonate solution, then with water, after which it was dissolved in hydrochloric acid and precipitated with ammonium hydroxide, and re-precipitated in order to get rid of the last traces of sodium; 100 grms. of the mineral were decomposed, and the chloride solution precipitated twice with sodium silicofluoride, once with sodium carbonate, and once with oxalic acid. The oxalate was ignited to oxide and weighed 0.0320 grm., equivalent to 0.03 per cent of the mineral. The fact that a precipitate was produced by sodium carbonate was pretty strong indication that eschynite contained scandium, but to test this point further the spark

spectrum of the chloride was studied. A Rowland grating was used and the second order spectrum photographed as a standard of comparison. The iron spectrum was photographed on one-half of the plate, and also served as a means of detecting the air lines, because these would show in both halves of the plate. The photographs were made of the portion of the spectrum which contained the strongest scandium lines, that is from 3500–5000, measured in Angstrom units. The wave lengths were then measured by projecting the lines on a screen, containing an accurately divided scale, from such a distance that the wave lengths of different known iron lines would fall on the proper scale divisions. When this was done the wave lengths sought could be read directly. As a result of this study no scandium lines were detected. There were few strong lines, leaving out those of platinum, but a larger number of dim lines. In general the latter corresponded very closely to the lines of yttrium and thorium, though it must be stated that some of the stronger yttrium and thorium lines were not noticed. The conclusion is that the substance which had been separated from eschynite by sodium silicofluoride and sodium carbonate was not scandium but a mixture of yttrium and thorium. A similar experiment was conducted with euxenite with like result, and scandium was not observed in samarskite.

(To be continued)

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

Ordinary Meeting, January 25th, 1912.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"Determination of the Coefficient of Interdiffusion of Gases and the Velocity of Ions under an Electric Force in Terms of the Mean Free Paths." By Prof. JOHN S. TOWNSEND, F.R.S.

A method is described by which an expression for the rate of interdiffusion of gases may be easily found, either on the ordinary supposition that the effect of a collision makes all subsequent directions of motion of the molecules equally probable, or without specifying in any way the effect of a collision.

Similar expressions are found for the velocity of ions under electric forces. In all cases the rate of diffusion of the ions is of the form  $K = \frac{1}{2}LV$  and the velocity under the electric force  $u = \frac{Xe}{m} \cdot \frac{L}{V}$ .  $L$  does not in general represent the mean free path, but it has the same meaning in both expressions, so that when an ion is moving under the action of a force and also by the process of diffusion its velocity is given by the equation—

$$u = -\frac{K}{u} \frac{du}{dx} + \frac{Xe}{m} \cdot \frac{L}{V}$$

or—

$$\frac{\frac{1}{2}mnV^2u}{K} = -\frac{mV^2}{3} \frac{du}{dx} + Xen,$$

or—

$$\frac{1}{K} (pu) = -\frac{dp}{dx} + nXe,$$

which is the well known form to which Maxwell's equation reduces when external electric forces are acting. The general equations for the motion of ions may thus be easily found from the rate of diffusion and the velocity under an electric force when these quantities are correctly determined.



"Note on the Scattering of  $\alpha$ -Particles." By Dr. H. GEIGER.

In a previous paper experiments were described on the scattering of the  $\alpha$ -particles by foils of various materials and thicknesses. The present note deals with a theoretical examination of the question. The scattering is considered as the result of a multitude of small deflections of the  $\alpha$ -particle by the individual atoms of the matter traversed.

The experimental curve of distribution with angle for a scattered pencil of  $\alpha$ -particles is found to be in good agreement with that derived from simple probability theory. The deductions also explain the experimental result that for thin foils, which do not appreciably alter the velocity of the  $\alpha$ -particles, the most probable angle of scattering varies as the square root of the thickness. To find the variation of the most probable scattering angle for large thicknesses of matter traversed, the change in velocity of the  $\alpha$ -particles has to be taken into account. Assuming, as found by experiment, that the most probable angle of scattering is inversely proportional to the third power of the speed, the theoretical curve is found to give a satisfactory explanation of the experimental results obtained with thick foils.

"The Effect of Temperature upon Radio-active Disintegration." By A. S. RUSSELL.

The effect of temperature upon the rate of decay, and the amount of  $\beta$ - and  $\gamma$ -ray activity, of radium emanation, of active deposit, and of radium C has been investigated. The results are entirely negative. All abnormalities of activity of  $\beta$ -rays obtained by previous authors, and by the author in this research, may be completely explained on two simple grounds.

The first of these is a change of distribution of radium C caused by its partial volatilisation inside the quartz tube at temperatures greater than  $320^\circ$ . The second is a change in the partition of radium C between the walls of the quartz envelope and the space enclosed.

At room temperature the greater part of the radium C is usually on the walls. At room temperature, after the tube has been cooled suddenly from high temperatures, it is entirely on the walls. Above  $650^\circ$  the radium C is distributed homogeneously throughout the volume of the tube. Each of these partitions gives a different  $\beta$ -ray ionisation in an electroscope, because the average path of the rays through the walls of the quartz envelope depends upon the partition. Under the conditions of experiment, radium B and radium C, and very probably radium A, may be completely volatilised inside sealed quartz tubes at a temperature of  $650^\circ$ . Radium B commences to volatilise at room temperature.

"Relation between Current, Voltage, Pressure, and the Length of the Dark Space in Different Gases." By F. W. ASTON and H. E. WATSON.

In a previous paper one of the authors has shown that in the discharge between large plain aluminium electrodes in gases at various pressures the following empirical equations are approximately true:—

$$D = \frac{A}{P} + \frac{B}{\sqrt{c}}, \quad V = E + \frac{F\sqrt{c}}{P};$$

where D is the length of the dark space, V the voltage between the negative glow and the cathode, c the current density, P the pressure, and A, B, E, F constants depending on the nature of the gas. The first part of the present communication gives the results of the continuation of this work, with the values of the constants for hydrogen, nitrogen, air, oxygen, carbon monoxide, helium, and argon.

The second part deals with a systematic investigation into the behaviour of the inactive gases when in a pure state. It was found that these gases behaved in an anomalous manner and by no means satisfied the above equations in general, but gave values in better agreement

with a third equation obtained by eliminating P from the two above. The results are described for helium, neon, argon, krypton, and xenon. Peculiar interest attaches to these gases in that all of them exhibit to a more or less striking degree the primary dark space recently discovered by one of the authors in hydrogen and helium. The behaviour of helium was exceedingly erratic, and seemed to indicate that this gas could support the discharge in two entirely different ways.

"Viscosities of Gaseous Chlorine and Bromine." By A. O. RANKINE, D.Sc.

By means of a method resembling in some respects that described by the author in earlier communications, the viscosities of chlorine and bromine have been compared with that of air. From these ratios the absolute values are deduced. The viscosities of chlorine having been obtained at two temperatures, it has been possible to calculate Sutherland's constant. The various values are as follows:—

| Gas.     | Temperature.           | Viscosity in C.G.S. units. |
|----------|------------------------|----------------------------|
| Chlorine | $12.7^\circ \text{C.}$ | $1.297 \times 10^{-4}$     |
| Chlorine | $99.1^\circ \text{C.}$ | $1.688 \times 10^{-4}$     |
| Bromine  | $98.7^\circ \text{C.}$ | $1.869 \times 10^{-4}$     |

The value of Sutherland's constant for chlorine is  $C = 325$ . The ratio of the critical temperature of chlorine ( $416^\circ \text{abs.}$ ) to this constant is 1.28, which is somewhat higher than the constant value (1.14) of the corresponding ratio for most gases; but this might be accounted for by the uncertainty of the exact value of C, arising from the smallness of the temperature range.

If the values of the viscosity of chlorine and bromine at corresponding temperatures are calculated, it is found that the squares of the viscosities are proportional to the respective atomic weights. (Corresponding temperatures signify those which bear equal ratios to the respective critical temperatures). In this respect chlorine and bromine appear to conform with the same rule as has been shown to hold for the inert gases.

"Testing of Plane Surfaces." By P. E. SHAW, B.A., D.Sc.

Scraped and lapped plane surfaces are found not only in surface plates supplied by the engineering trade, but also in several apparatus of precision, e.g., interferometers and measuring-machines. It is quite possible that the errors of these surfaces may be the determining factor in the accuracy of the measurement made in using these apparatus. Yet up to the present there seems to have been no simple device for measuring these errors. To supply this want, two forms of surface-tester have been made by the writer:—

(a) A stout wooden bar, 16 inches long, has twin feet half-inch apart at one end, whilst there is a third foot at the far end. Midway between the twin feet at one end and the third foot at the other is a micrometer screw. The instrument acts on the spherometer principle, but contact is made electrically with a telephone in circuit.

(b) A steel bar, 12 inches long, has 1 foot  $\frac{1}{4}$ -inch diameter at one end and a similar foot at the other end, whilst midway between the feet is the end of a micrometer screw. Contact is generally made mechanically. This instrument must be made very carefully, the flat surfaces of the two feet and of the micrometer end being in one position truly in one plane.

(b) is made in duplicate, so that by using first one tester and then the other on one place of a surface, and then "fitting" them together, the actual departure of the surface from planeness can be found. These testers read to  $1/10,000$ th inch, and have an error on one reading of about that amount. Investigations have been made on a considerable number of "surface plates" and "straight edges" as supplied by the engineering trade. A bad plate shows errors of about  $1/2000$ th inch from true plane, an average one only  $1/5000$ th inch, and some special ones of

small size, recently made, had a figure of only  $1/10,000$ th as indicated by tester (b).

Tests were also made by these instruments on many samples of plate glass, for which the errors varied from  $1/3000$ th inch to  $1/300$ th inch on a length of 12 inches. Thus we have a means of revealing a surface out of truth, whether due to faulty making or to warping with lapse of time.

"*Antelope Infected with Trypanosoma gambiense.*" By Capt. A. D. FRASER, R.A.M.C., and Dr. H. L. DUKE.

## CHEMICAL SOCIETY.

Ordinary Meeting, January 18th, 1912.

Prof. PERCY F. FRANKLAND, LL.D., F.R.S., President, in the Chair.

MESSRS. Rufus Gaunt and Harold King were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Clement William Bailey, M.Sc., Evington, Leicester; James Ewart Bridge, B.Sc., Sarnia, Hatfield Road, Ipswich; William Thomas Clarke, B.Sc., Mansfield Road, Heanor, Derbyshire; Surendranath De, 21, Srigopal Mullick Lane, Calcutta, India; Wilfrid James Fleet, Imatra, King's Road, Bournemouth; Isidor Morris Heilbron, Ph.D., 7, Claremont Terrace, Glasgow; Charles James, New Hampshire College, Durham, N.H., U.S.A.; James William McMyn, 35, Snowdon Road, Eccles, Manchester; Pestanji Manekji Modie, B.A., Meher Buildings, Tardeo, Bombay, India; Richard Gillies Neilson, Burna Oil Co., Ltd., Rangoon, Burma; John Wilfred Parkes, 14, Gower Terrace, Willenhall, Coventry; Edgar Alexander Rayner, B.Sc., 71, Welldon Crescent, Harrow; Henry Edgar Smith, M.Sc., The Mount, Dawley, Salop; Percy Rudolph Strivens, The Crofts, Horbury, Wakefield; Forsyth James Wilson, D.Sc., Ph.D., 96, Great George Street, Glasgow.

The PRESIDENT announced that the Moissan Memorial Lecture would be delivered by Sir William Ramsay, K.C.B., LL.D., F.R.S., on February 29th, 1912, at 8.30 p.m.

Of the following papers those marked \* were read:—

\*1. "*Photophosphorescence of Inorganic Solid Solutions.*" By A. LIONEL LANDAU.

A study of the literature of phosphorescent inorganic solid substances leads one to the belief that in cathodophosphorescence the phosphorogen is in solid solution, the particular kind of solid solution being colloidal; this theory explains the variation of the colour of the luminescence that a given phosphorogen imparts to different solvents, and also explains the variation of the colour of the luminescence of a given substance at different temperatures.

Cathodophosphorescent substances are not necessarily photothermoluminescent substances, and the theory was propounded that the latter property is due to the presence of colloidal highly positive element in solid solution in addition to colloidal phosphorogen.

The work already published on fluor-spar and zinc sulphide confirms this theory, and it was shown on experimental grounds that it is quite possible that the particular varieties of the alkaline earth sulphides known as "phosphorescent" also contain colloidal positive element. Evidence was adduced against any other theory so far propounded.

It was further suggested on experimental grounds that the flux necessary in alkaline-earth sulphides acts by rendering the sulphide translucent, and the conclusion was drawn that photothermoluminescence can only be exhibited by substances which are translucent or transparent

and contain colloidal phosphorogen and colloidal highly-positive element in solid solution.

## DISCUSSION.

In reply to the President, Mr. LANDAU said that the authority for the statement that calcium is produced by the reaction between lime and carbon was Moissan (*Ann. Chim. Phys.*, 1899, [7], xviii., 289). Calcium carbide was produced when the carbon was in excess; it was not, so far as he knew, phosphorescent.

\*2. "*The Preparation of Conductivity Water.*" By FERDINAND BERNARD THOLE.

The two best known forms of apparatus for the preparation of conductivity water, namely, those designed by Bousfield and by Hartley, Campbell, and Poole, both suffer from two disadvantages, namely, (1) the condenser is somewhat complex and expensive, and (2) as the water is completely cooled before collection the removal of the carbon dioxide and ammonia from the apparatus is slow.

The author described two inexpensive forms of apparatus (one of which may be readily constructed from ordinary laboratory materials), a common feature of which is that steam may be blown through the collected water, thus rapidly removing dissolved gases. The water obtained has an average conductivity of  $1.3-1.2$  gemmhos ( $25^\circ$ ), and therefore compares favourably with that obtained under similar conditions by Bousfield's apparatus.

## DISCUSSION.

Dr. DUNSTAN pointed out that he had used Mr. Thole's apparatus during the past two years, and had found it most efficient, not only for the purpose it was immediately designed to fulfil, but also for providing a copious supply of pure dust-free water for physico-chemical experiments.

Mr. THOLE agreed with the President that part of the conductivity of the water obtained was due to dissolution of alkali from the glass condenser and receiving flask, especially as those surfaces were exposed for a short time to the action of boiling water.

The object in view, however, was to design a simple and inexpensive apparatus which would yield water sufficiently pure for most ordinary work. Further purification could only be attained by increasing the cost and complexity of the apparatus.

3. "*The Boiling-points of Mercury, Cadmium, Zinc, Potassium, and Sodium.*" By CHARLES THOMAS HEYCOCK and FRANCIS EDWARD EVERARD LAMPLOUGH.

During the course of some work now in progress, the authors had occasion to determine the boiling-points of mercury, cadmium, zinc, potassium, and sodium at different pressures. Below are given the values for the boiling-points under a pressure of 760 mm. The temperatures were in all cases determined by means of platinum resistance pyrometers. The temperatures assumed in calibrating the pyrometers were ice, steam, and the boiling-point of sulphur,  $444.53^\circ$  (Callendar and Griffiths):—

|                 | Boiling-point. | Change in b. p. per mm. at $760^\circ$ . |
|-----------------|----------------|------------------------------------------|
| Mercury .. ..   | $356.7^\circ$  | $0.0746^\circ$                           |
| Cadmium .. ..   | $765.9$        | $0.12$                                   |
| Zinc .. ..      | $905.7$        | $0.133$                                  |
| Potassium .. .. | $762.2$        | $0.135$                                  |
| Sodium .. ..    | $882.9$        | $0.153$                                  |

4. "*Formation and Reactions of Imino-compounds. Part XVII. The Alkylation of Imino-compounds.*" By JOCELYN FIELD THORPE.

Evidence was recorded in support of the following generalisations:—

1. Compounds containing the complex  $CX_2:CR:CH_2X$ , in which X may be any negative group and R any univalent radicle or group, react with sodium ethoxide so as to retain the mobile hydrogen atom, and, therefore yield sodium derivatives of the type  $CX_2:CR:CHNaX$ , in which



the mobile hydrogen is represented by an asterisk. The displacement of the sodium in this compound by an alkyl group yields an alkyl derivative,  $CX_2 \cdot CR \cdot CH(Alk)X$ , and the action of sodium ethoxide on this substance causes the displacement of the mobile hydrogen atom, but the metal then takes up the most negative position in the system, yielding the sodium derivative,  $CNaX_2 \cdot CR : C(Alk)X$ .

2. The imino-compounds react with sodium ethoxide in their amino-form only. They are then derivatives of glutaconic ester, and as such conform to the above generalisation.

5. "1:2-Diketohydrindene." By WILLIAM HENRY PERKIN, jun., WALTER MORRELL ROBERTS, and ROBERT ROBINSON.

The authors showed that 1:2-diketohydrindene,  $C_6H_4 \begin{smallmatrix} CO \\ \diagup \diagdown \\ CH_2 \end{smallmatrix} > CO$ , may be prepared from isonitroso- $\alpha$ -hydrindone by treatment with hydrochloric acid in the presence of formaldehyde, and the properties of this substance and those of several of its derivatives were described.

6. "iso-Narcotine." By ERNEST GRIFFITHS JONES, WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

In order to obtain further evidence in support of the formula suggested for this alkaloid by Perkin and Robinson (*Trans.*, 1911, xcix., 777), the authors described some experiments on the condensation of phthaldehydic acid and its opianic acid with resorcinol dimethyl ether and catechol dimethyl ether in the presence of hydrochloric acid.

7. "Esterification Constants of some Substituted Acetic and Benzoic Acids." By JOHN JOSEPH SUDBOROUGH and MARGARET KATHLEEN TURNER.

The esterification constants of a number of substituted acetic and benzoic acids have been determined at 15° and 20°, using hydrogen chloride as catalyst.

The relative retarding effects of different substituents are not necessarily the same in the two series.

Acetophenone *o*-carboxylic and *o*-phenoxybenzoic acids are esterified more readily than benzoic acid.

Hydrogen fluoride is a feeble catalyst as compared with hydrogen chloride.

8. "Aromatic Antimony Compounds. Part III. Primary Aryl Derivatives." By PERCY MAY.

Phenylstibinic acid,  $C_6H_5 \cdot SbO(OH)_2$ , was prepared according to Hasenbäumer's method (*Ber.*, 1898, xxxi., 2910), but the product was contaminated with diphenylstibinic acid ( $C_6H_5)_2 SbO \cdot OH$ . A modification of the method led to the production of pure phenylstibinic acid. The mixture of phenylstibinic and diphenylstibinic acids on nitration yields a mixture of nitro-compounds, from which, by re-crystallisation from glacial acetic acid, di-m-nitrodiphenylstibinic acid was obtained in yellow needles melting at 210–213° (compare Morgan and Micklethwait, *Trans.*, 1911, xcix., 2294). Reduction of *m*-nitrophenylstibinic acid yielded a small quantity of *m*-antimonylaniline,  $NH_2 \cdot C_6H_4 \cdot SbO$ , a light yellow powder, insoluble in water and alkali, soluble in hydrochloric acid. This compound has a powerful irritant action on the mucous membrane. *m*-Aminophenylstibinic acid,  $NH_2 \cdot C_6H_4 \cdot SbO(OH)_2$ , is produced by the gentle oxidation of this substance, and a very small quantity was isolated in the form of its chloride. The sodium salt was also obtained, but not in a pure condition.

9. "The Aryl Ethers of Glycide, Glycerol, and Glycerol- $\alpha$ -monochlorohydrin." By ERNEST ROBERT MARLE.

The action between epichlorohydrin and the sodium derivative of a phenol was reviewed, and the methods of preparation described by Lindeman (*Ber.*, 1891, xxiv., 2145), Boyd (*Trans.*, 1901, lxxix., 1221), and Boyd and Marle (*Trans.*, 1908, xciii., 838) for glycide ethers and

diaryl glycerol ethers, and that described by Boyd and Marle (*Trans.*, 1910, xcvi., 1788) for the aryl ethers of glycerol- $\alpha$ -monochlorohydrin have been used to prepare a number of these derivatives so as to complete the series, as far as possible, in the case of some of the more important phenols. The phenylurethanes of the aryl ethers of glycerol- $\alpha$ -monochlorohydrin were also described.

Several new monoaryl ethers of glycerol have been prepared by the action of the sodium derivative of a phenol on glycerol- $\alpha$ -monochlorohydrin.

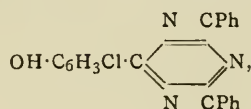
Evidence was adduced to show that the action of concentrated hydrochloric acid on a glycide ether is to produce  $\gamma$ -chloro- $\beta$ -hydroxy- $\alpha$ -aryloxypropane, the isomeric  $\beta$ -chloro- $\gamma$ -hydroxy- $\alpha$ -aryloxypropane being formed, if at all, only in very small amount.

10. "The Action of Ammonia on 6-Chloro-2-phenyl-1:3-benzoxazine-4-one." By ERNEST CHISLETT HUGHES and ARTHUR WALSH TITHERLEY.

Similar observations have been made as to the action of ammonia on 6-chloro-2-phenyl-1:3-benzoxazine-4-one,

$C_6H_5Cl \begin{smallmatrix} CO \cdot N \\ \diagup \diagdown \\ O - CPh \end{smallmatrix}$ , to those in the case of the parent ring compound devoid of chlorine.

A bright yellow crystalline compound, 5-chlorosalicylbenzamidine,  $OH \cdot C_6H_3Cl \cdot CO \cdot N : CPh \cdot NH_2$ , results through rearrangement of the intermediate additive ring-compound formed. By long-continued action of ammonia, 5'-chloro-2'-hydroxy-2:4:6-triphenyl-1:3:5-triazine,



is obtained as a pale yellow solid, and the same compound is produced with great rapidity by the action of benzamidine on 6-chloro-2-phenyl-1:3-benzoxazine-4-one. It is also produced more slowly from benzamidine and phenyl 5-chlorosalicylate or 5-chlorosalicylbenzamidine.

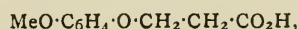
11. "The Thio-analogues of Coumarin and its Derivatives." By ARTHUR CLAYTON and WILLIAM GODDEN.

Certain nitrothiocoumarins were prepared by heating the corresponding nitrocoumarins with xylene and phosphorus pentasulphide, and their identities established by partial oxidation, which in each case yielded the parent nitrocoumarin. The ketonic structure present in the thiocoumarins was shown to be preserved in their nitro-derivatives, as the latter compounds yield oximes and hydrazones. The nitrothiocoumarins possess a deep golden colour, thus differing from the nitrocoumarins, which are white; the yellow colour, heretofore stated to characterise 8-nitrocoumarin, was shown to be due to the presence of an impurity.

12. "Experiments on the Synthesis of Brazilin and Hæmatoxylin and their Derivatives." (Preliminary Note). By WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

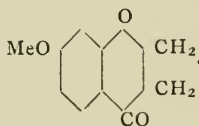
The publication by Tschitschibabin and Nikitin (*Journ. Russ. Phys. Chem. Soc.*, 1911, xliii., 1185) of a note on 3-methoxydihydro-1:4-benzopyrone leads the authors to submit the results of a research on the same subject, on which they have been engaged at intervals during the last two years.

*m*-Methoxy- $\beta$ -phenoxypropionic acid,



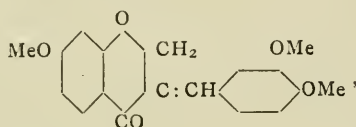
was obtained by the interaction of resorcinol monomethyl ether and  $\beta$ -iodopropionic acid in aqueous alkaline solution, and also by the hydrolysis of the ester resulting from the condensation of sodio-resorcinol monomethyl ether and

ethyl  $\beta$ -iodopropionate. It crystallises from water in shining leaflets melting at  $82^\circ$ , and dissolves in nitric acid to an intense green solution, which becomes bluish green after dilution with water. On treatment with phosphoric oxide in benzene solution, under the same conditions as were used for the preparation of dimethoxyhydrindone (*Trans.*, 1907, xci., 1080), this acid is easily converted into 7-methoxy-2 : 3-dihydro-1 : 4-benzopyrone (7-methoxy-chromanone),



The ketone is best purified by distillation, and boils at  $197^\circ/30$  mm. It crystallises from light petroleum in colourless needles melting at  $56^\circ$ . The semicarbazone crystallises from alcohol in small glistening plates, melting and decomposing at  $222^\circ$ .

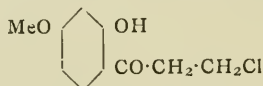
*Veratrylidene-7-methoxychromanone*,



is closely related to trimethylbrazilin, and is obtained by treatment of equimolecular quantities of methoxychromanone and veratraldehyde in methyl alcohol with potassium hydroxide. It consists of almost colourless needles, and can be easily crystallised from ethyl or methyl alcohols. It is rather sparingly soluble, melts at  $140^\circ$ , and dissolves in sulphuric acid to an intense crimson solution. Indications have already been obtained that it is possible to convert this substance into a derivative of brazilin.

The poor yield obtained in the preparation of methoxyphenoxypionic acid led the authors to investigate other methods of preparation of methoxychromanone, but up to the present time they are unable to dispense with that described above.

*o*-Chloro-2-hydroxy-4-methoxypropiofeune,



is produced by the condensation of resorcinol dimethyl ether and  $\beta$ -chloropropionyl chloride in light petroleum solution in the presence of anhydrous aluminium chloride. It crystallises from methyl alcohol in groups of colourless needles. On heating, it softens at  $98^\circ$ , and undergoes no further change until the almost liquid substance becomes transparent at  $138^\circ$ . Decomposition also occurs at this temperature. It gives a violet coloration with ferric chloride, and has the irritating properties of chloro-ketones.

On treatment with alkalis the production of methoxychromanone was expected, but instead a substance is quantitatively produced, which crystallises from ethyl acetate in colourless needles melting at  $249-250^\circ$ . The nature of this compound has not yet been completely elucidated.

13. "The Influence of Solvents on the Rotation of Optically Active Compounds. Part XVII. The Relationship between the Chemical Constitution and the Influence of a Solvent." By THOMAS STEWART PATTERSON and ELIZABETH FINDLAY STEVENSON.

The influence of a number of solvents in modifying the rotation of an optically active ester was described and discussed in connection with the chemical constitution of the solvent.

## PHYSICAL SOCIETY.

Ordinary Meeting, January 26th, 1912.

Prof. H. L. CALLENDAR, F.R.S., President, in the Chair.

AN exhibition of a Direct Reading Instrument for Submarine Cable and other Calculations was given by Mr. R. APPELYARD.

The logarithmic spiral has frequently been used for determining by a graphic method the logarithm of the ratio of two quantities. In acoustics, for example, it has been of service as a convenient means of demonstrating the way in which "frequency" is associated with "interval." If an attempt is made to apply the spiral to the solution of practical engineering problems, such as arise in the design of submarine cables, there is difficulty in obtaining sufficient accuracy, especially for readings near the pole of the spiral. The author has removed this defect by introducing a secondary spiral, similar in all respects to the primary spiral, and having the same pole, but displaced round the pole through a certain constant angle. In this instrument a pair of radial scales, each having its zero at the pole, and each divided into the same number of equal divisions, can be rotated about the pole. At all angular positions a scale of this kind will be cut by the two spirals if they are sufficiently extended. It has been proved by the author that for all angular positions of such a radial scale, the distance between the pole and the point where that radial scale is cut by the secondary spiral is always the same multiple of the distance between the pole and the point where the radial scale is cut by the primary spiral. In effect, therefore, the secondary spiral magnifies the radial scale readings of the primary spiral to any desired extent, depending only upon the angle through which the template of the primary spiral is rotated to form the secondary spiral. In the instrument exhibited the spirals are drawn in a manner that avoids ambiguous readings, and that gives maximum precision within the range of diameters of conductors and dielectric coverings required for submarine cable work. The instrument is provided with two similarly divided radial scales, one corresponding to  $d$ , the diameter of the conductor, and the other corresponding to  $D$ , the diameter of the dielectric. The angle between the two scales, corresponding to any pair of values of  $d$  and  $D$ , is then a measure of  $\log D/d$ . The scales can be marked to indicate weights of conductor and dielectric, and the circle of degrees to which the spiral is drawn can be marked to indicate  $\log D/d$ , capacity, dielectric resistance, and other functions of  $D$  and  $d$ , if required, for any definite dielectric, the specific constants of which are known.

The general equation to the spiral may be written—

$$\theta = A \log d + B,$$

where  $A$  and  $B$  are constants. Hence when  $d_{\min.}$  and  $D_{\max.}$  are both on the  $0^\circ$  radius vector, any two points  $d$ ,  $D$  on the spiral are associated with their corresponding angles  $\theta_d$   $\theta_D$  in degrees by the three equations—

$$\theta_d = A \log \frac{d}{d_{\min.}} \dots \dots \dots (1)$$

$$\theta = A \log \frac{D}{D_{\max.}} + 360,$$

$$A = \frac{360}{\log \frac{D_{\max.}}{d_{\min.}}}$$

To draw the secondary spiral, the primary spiral is rotated backwards about its pole through an angle  $\phi$ . This is equivalent to rotating both the radial scales through  $\phi$ . The intercepts are now  $d_1$  and  $D_1$ —i.e., the radial scale readings are now greater in the ratio—

$$n = \frac{d_1}{d} = \frac{D_1}{D}.$$



Equation (1) then becomes—

$$\theta_d + \phi = A \log \frac{d_1}{d_{\min.}} \dots \dots (2)$$

Subtracting (1) from (2)—

$$\phi = A \log \frac{d_1}{d} = A \log n,$$

which gives  $\phi$  for any required magnification  $n$ .

#### DISCUSSION.

Prof. S. P. THOMPSON remarked on the useful applications of the instrument, and asked if it would be possible to make it up in a cylindrical form instead of on a plane.

Dr. A. RUSSELL pointed out the large number of calculations in which the logarithm of the ratio of two quantities occur.

The AUTHOR, in reply, thought it would be rather difficult to apply the instrument to a cylinder. In cable calculations he used it for finding the capacity and dielectric resistance per mile. By clamping the radial arms and rotating them, an infinite number of values for the diameter of the conductor and the insulation could be picked out that would give the same capacity and dielectric resistance per mile, and therefore the same speed of signalling.

A paper on "*The Vibration Galvanometer and its Applications to Inductance Bridges*," was read by Mr. S. BUTTERWORTH.

Vibration galvanometers are divided into two types according as their moving parts possess only one or an infinite number of degrees of freedom. A theory of the former type of galvanometer when used in circuits containing inductance and capacity is completely worked out, and the conditions of maximum sensibility are determined.

The same theory is shown to be applicable to the string type of galvanometer provided that the damping is small. The effect of harmonics is also considered in this case.

The results are applied in the case of a general inductance bridge, which includes: (a) Anderson's bridge, (b) a modified Rimington's bridge, (c) Heydweiller's modification of the Carey-Foster bridge, and (d) a bridge for measuring frequency.

The best conditions for working Anderson's bridge with the vibration galvanometer as detector are obtained.

Experimental results for methods (b) and (d) are quoted, the latter method being used to calibrate a Duddell vibration galvanometer for frequency.

#### DISCUSSION.

Mr. A. CAMPBELL pointed out that though the current sensitivity could be increased by decreasing the damping, the voltage sensitivity was not affected as the effective resistance was thereby increased. The voltage sensitivity was also independent of the control couple and the inertia of the moving system.

Mr. W. DUDELL said that vibration galvanometers might be looked upon as alternate-current motors, and to be efficient must be capable of producing a strong back E.M.F.

Dr. A. RUSSELL pointed out that for high frequencies the assumption that the damping was proportional to the velocity might introduce errors into the calculation.

A paper "*On Sealing Metals*," was read by Dr. P. E. SHAW.

The established method of fixing quartz fibres for accurate torsion experiments is due to Prof. C. V. BOYS. It involves careful cleaning, silvering, electrolytic deposit of copper, tinning, and finally soldering. This considerable trouble can be avoided by the simple means given below, while the resulting joint is in some cases stronger. Prof. Threlfall used Margot's solder (92 per cent Sn, 8 per cent Zn) to fasten glass, aluminium, or quartz surfaces to any other. The writer finds this material acts perfectly, and is very simple, the bit being of aluminium, and there

being no flux. Further investigation shows that there is no special merit in Margot's formula. In place of Margot's solder the following will be found to act very well: (a) Tin, (b) zinc, (c) various alloys of tin and zinc, (d) tinman's solder, and (e) aluminium. Lead does not stick well, though it might be made to do so if oxidation were prevented. Then there is a variety of materials with melting-point ranging from 180° to 660°. For all these and like materials which act in the same manner as sealing-wax the writer suggests the term sealing-metals. They have the advantages over any wax in (a) high melting-point, and (b) non-emission of vapour when temperature is raised.

There are obvious applications other than for tension fibres where joints to withstand temperature are required.

#### DISCUSSION.

The PRESIDENT stated that the method would be extremely useful to physicists if it could be used for making vacuum-tight joints that would stand a high temperature.

Mr. A. CAMPBELL mentioned that metals could be soldered to glass by first platinising the glass.

Mr. W. DUDELL stated that he had successfully fixed quartz fibres with ordinary solder.

Mr. R. APPELYARD thought that condensers could be made to keep more constant in capacity if the tinfoil could be adhered to the mica.

Mr. A. CAMPBELL stated that silvered mica condensers had been made, but were not so reliable as the ordinary tinfoil ones. This was probably due to the very sharp edge of the silver. Perhaps platinised mica would give better results.

The AUTHOR, in reply, stated that metals were very much more porous than glass, so too much must not be expected from joints made with fusible metals. He said it was desirable to find a sealing-metal having a small coefficient of expansion, for this would have a better chance of adhering strongly after solidification. He thought Mr. Appleyard's suggestion valuable. There should be no difficulty in building up a condenser made on those lines.

A paper on "*A Negative Result connected with Radio-activity*," by Dr. J. H. VINCENT and Mr. A. BURSILL, was taken as read.

Specimens of iron, antimony, and bismuth were subjected to a high-frequency alternating magnetic field. The air in the neighbourhood was tested for any ionisation that might have been thus produced. The results were negative.

A paper on "*A Copper Zinc Uranium Oxide Cell and the Theory of Contact Electromotive Forces*," by Prof. A. ANDERSON, was also taken as read.

A uranium oxide cell with copper and zinc plates is described, and reference is made to the temperature coefficient of its E.M.F. A difficulty connected with the energetics of the cell is pointed out, and a possible explanation put forward tentatively.

Decomposition of Azines by Heat.—Paul Pascal and Léon Normand.—Nearly all azines fuse without undergoing decomposition even in the naphthalene series, in which the melting-point is above 300°. Above the melting-point, and at a temperature which varies according to the azine in question, gases are always evolved in increasing quantities as the temperature rises. In the aromatic azines in which the aldehyde group is directly attached to the radical this decomposition is particularly regular. Thus an azine of the type  $R-CH-N_2-CH-R'$ , e.g., benzalazine, first loses nitrogen, giving the stilbene derivative  $R-CH=CH-R'$ . At high temperatures hydrogen is evolved simultaneously, almost entirely in the form of ammonia and hydrocarbons, and nitrogen compounds of complex nuclear structure are formed.—*Bull. Soc. Chim. de France*, ix.-x., No. 23.

## NOTICES OF BOOKS.

*Who's Who in Science*, 1912. Edited by H. H. STEPHENSON.  
London: J. and A. Churchill.

THIS annual is not simply a collection of names of prominent men of science, as its title would lead one to expect; but, in addition to the names and positions of a great many prominent men, much other useful information has been added. Almost the first page contains the Obituary for 1911—a sad list indeed, but at the same time a useful one. It is, however, to be regretted that the dates of death and other particulars have been omitted. Following is a list of the world's Universities, with the names of the principal Officers and Senior Professors. Then come the Biographies, occupying some 276 pages; the names are arranged in alphabetical order, and at the end of the book there is a classified index, giving the departments and countries to which the names refer. It is exceedingly easy to find any name that is included—the pity is that there is so little of it; as an instance, for "London" only four Colleges are given, occupying less than half a page, while in the "Minerva" of Dr. K. Trübner the list of scientific Institutions and Officers in "London" occupies some 37 pages. The need for a comprehensive work of this description in English is unquestionable, and we hope that "Who's Who in Science" may soon be greatly extended.

*La Molécule Cyclique*. ("The Cyclic Molecule"). By ANIBAL CHACÓN. Montevideo: Juan J. Dornaleche. 1911.

IN this pamphlet the author puts forward a hypothesis to explain the relation between the cyclic and acyclic series, and further extends it to the cases of allotropy and polymerisation. He points out, not by any means for the first time, the objection to Kekulé's benzene formula, and suggests a modified constitution formula which certainly explains the existence of isomeric forms of benzene hexachloride. He then considers the cases of more complex molecules, *e.g.*, naphthalene, anthracene, &c., and explains the general applicability of his theory, which may be chiefly stated as follows:—The simplest molecule of a cyclic substance consists of three sub-molecules which mutually saturate one another. More complex cyclic molecules are formed by the union of two or more simple cycles. An element can exist in two or more states, differing from one another in the number of atoms contained in the molecule, and polymerisation is due to the formation of molecules from two or more primitive molecules mutually saturating one another. It will be seen that the hypothesis is not new in its broadest outlines, but the author has some suggestions to offer in explanation of certain anomalies in isomerisation.

*La Nuova Fisica*. ("The New Physics"). By AUGUSTO RIGHI. Bologna: Nicola Zanichelli. 1912.

THE meeting of the Italian Society for the Advancement of Science held at Rome in October, 1911, was particularly fortunate in having the opportunity of hearing Prof. Righi deliver the Inaugural Address on the New Physics. The address, which is now published in book form, was full of stimulating suggestions as to the directions in which physical research is tending, and the author has done so much to further the advance of physical knowledge that he is entitled to speak with authority on what has already been done, and to demand the most careful attention for his prophecies concerning future work. Within the necessarily restricted limits of an address he was naturally unable to do more than allude to several important questions; but all he has to say is illuminating, and his accounts of the development of modern conceptions of physical phenomena will be read with interest by the general public as well as by students of science.

## CORRESPONDENCE.

## REDUCTION OF SILVER CHLORIDE.

To the Editor of the Chemical News.

SIR,—In reply to Mr. Godbole's letter (CHEMICAL NEWS, vol. civ., p. 173) I may first state that the intention of my article (CHEMICAL NEWS, vol. ciii., p. 288) was to make known a ready method of converting silver chloride into a form easily convertible to silver nitrate—so, as a matter of fact, for my purpose it really was immaterial at the time what the composition of the residue after the peroxide treatment might be, provided that the precipitate was completely soluble in nitric acid. Mr. Godbole found that his precipitate fulfilled this condition.

On again trying the method it was found that the precipitate obtained was almost, if not entirely, all metallic silver. This statement is based on the following experiments:—Separate portions of the freshly precipitated substance was heated with 10 E and 20 E ammonium hydrate respectively, and in neither case was any silver found in solution; also, on treating a portion with sodium thiosulphate no silver could be detected in the solution. These experiments would point to the absence of the oxide.

Another experiment was tried. The precipitate was first dried below 100° C., then rubbed in an agate mortar with an agate pestle. The grey mass assumed the lustre of metallic silver, and formed metallic streaks on the mortar where the pestle was drawn across; also the substance, when treated with 8 E HNO<sub>3</sub>, readily dissolved in the cold with evolution of red fumes.

Mr. Godbole says: "After the addition of the solution of Na<sub>2</sub>O<sub>2</sub> the mixture was boiled, &c." Unless we suppose this statement of his method of carrying out the reduction to be a typographical error, then it is at this point that his procedure differs from mine, inasmuch as I add the ammoniacal silver solution to the solid sodium peroxide, as he may find by referring to the original article.

The difference caused is possibly due to the fact that little or no Na<sub>2</sub>O<sub>2</sub>, or even H<sub>2</sub>O<sub>2</sub>, would be in the liquid after treatment of Na<sub>2</sub>O<sub>2</sub> with water, especially if the solution became heated; whereas by adding the silver solution to the solid peroxide, the resulting reducing agent or agents are in the immediate vicinity of the silver compound, and can thus be utilised fully.—I am, &c.,

EDGAR H. BOOTH.

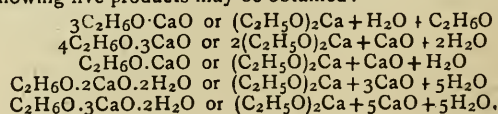
Sydney University, Australia,  
January 2nd, 1912.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless other is expressed.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences*. Vol. cliii., No. 26, December 26, 1911.

Calcium Ethylates.—M. de Forcrand.—When alcohol reacts with a metal of the alkaline earths, or with a hydride, acetylde, or amide of such a metal, an ethylate is obtained, *e.g.*, (C<sub>2</sub>H<sub>5</sub>O)<sub>2</sub>Ca. These alcoholates show a great tendency to fix excess of alcohol. Thus a compound of formula (C<sub>2</sub>H<sub>5</sub>O)<sub>2</sub>Ca + 2C<sub>2</sub>H<sub>6</sub>O is readily formed. If attempts are made to remove the excess of alcohol the following five products may be obtained:—





**Electrical Resistivity of Special Steels.**—O. Boudouard. In carbon steels the electrical resistivity increases with the percentage of carbon. In nickel steels containing equal proportions of nickel carbon considerably augments the value of  $\rho$ , while with manganese steels no such effect is observed. Chromium steels show great irregularities whether much or little carbon is present.

**Method of Separating Phosphomolybdates from Silicomolybdates.**—P. Mélikoff.—The molybdic reagent is generally used to separate traces of phosphoric acid in minerals and rocks. It has the disadvantage of also precipitating silicic acid. But although the phosphomolybdates and silicomolybdates are very similar they may be separated by a method based upon their different solubilities in  $H_2O_2$ . Thus a mixture of equal volumes of 30 per cent hydrogen peroxide and 8 per cent ammonium molybdate in nitric acid does not dissolve a trace of silicomolybdate, while phosphomolybdate is readily soluble in it.

**Molecular Weight of Lime: Atomic Weight of Calcium.**—Oechsner de Coninck.—The author has determined the molecular weight of lime by preparing pure calcium formate from lime and formic acid and converting it into the oxide by heating. The mean of five experiments gives the molecular weight 56.02 for lime and 40.02 for the atomic weight of calcium.

**Solubility of Uranous Oxide in Acids.**—A. Raynaud.—The acids HCl, HBr,  $H_2SO_4$ ,  $HNO_3$ ,  $CH_3COOH$ , and aqua regia have only very slight action on  $UO_2$ . Even with the concentrated acids solution takes place very slowly, and in some cases only at the expense of the oxygen of the air or of the solvent. Aqua regia and nitric acid yield uranic salts.

**Hypochlorous Amides.**—E. Boismenu.—The chlorinated amides obtained by the action of hypochlorous acid on amides are hypochlorous amides. Monohypochlorous or dihypochlorous amides are obtained according to the proportions of amide and water used. The former are solids, and the latter yellow, very unstable liquids, being more unstable the lower their molecular weights. They are converted into the monohypochlorous amides by the addition of the calculated amount of amide, and they react with a solution of potassium iodide, liberating 4 atoms of iodine for every two atoms of chlorine contained in their molecule.

**Three Normal Saturated Hydrocarbons: Triacotane, Tetratriacontane, and Hexatriacontane.**—A. Gascard.—Phosphorus iodide transforms pentadecylic alcohol into the hydriodic ether, which on treatment with sodium in presence of xylol gives the hydrocarbon triacotane,  $C_{30}H_{62}$ . The pentadecylic alcohol may be obtained by triturating silver palmitate with iodine, purifying the palmitate of pentadecyl thus formed, and saponifying. When silver stearate is treated similarly, tetratriacontane,  $C_{34}H_{70}$ , is obtained, and hexatriacontane,  $C_{36}H_{74}$ , may be prepared by treating octadecyl iodide with sodium.

**Action of Caustic Potash on Primary Alcohols.**—Marcel Guerbet.—The oxidation of a primary alcohol by means of caustic potash always produces the corresponding acid. This method of oxidation is very effectual, the yield being 95 per cent for the alcohol containing  $C_6$ , and nearly theoretical for higher alcohols. The oxidation can be carried out equally well in an open vessel or a sealed tube.

Bulletin de la Société Chimique de France.  
Vol. ix.-x., No. 24, 1911.

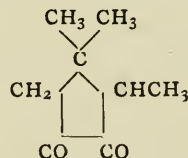
**Coefficient of Magnetisation of Gold.**—M. Hanriot and F. Raoult.—When an alloy of gold and silver is attacked by nitric acid the gold remains in a spongy mass, "brown gold," which is formed of a mixture in variable proportions of ordinary or  $\alpha$ -gold and a new modification,  $\beta$ -gold. Fused gold, which seems to consist only of the

$\alpha$  variety, is diamagnetic, and  $\beta$ -gold has not the same coefficient of magnetisation as  $\alpha$ -gold.

**Systematic Analysis of Phenol Compounds.**—J. A. Sauchez.—The following tests may be applied to detect the presence of any of the following phenols in a mixture:—Pyrocatechin, resorcin, hydroquinone, pyrogallol, phloroglucin, salicylic acid, gallic acid, tannic acid, vanillin. (1) A slate-coloured or brown precipitate with acid mercuric nitrate shows the presence of pyrocatechin. (2) The solution is precipitated with lead acetate and filtered. If the filtrate gives a pink flocculent precipitate with formol hydrochloric acid, resorcin is present; or (3) if it gives an indigo blue coloration with sulphomolybdic acid, hydroquinone is present. (4) A red coloration when the lead acetate precipitate is treated with formol hydrochloric acid shows the presence of pyrogallol. (5) Furfural and HCl give a green coloration with phloroglucin. (6) If the solution is precipitated with lead nitrate and HCl, and ferric chloride are added to the filtrate, a violet coloration shows the presence of salicylic acid. (7) KCN gives a ruby coloration with gallic acid. (8) Nicotine gives a persistent white precipitate with tannic acid. (9) Phloroglucin and HCl give a ruby coloration with vanillin.

**Decomposition of Aldazines by Heat.**—Paul Pascal and Léon Normand.—The asymmetric azine benzal hydrazine decomposes as regularly as benzalazine and its symmetric homologues, giving a 30–35 per cent yield of paramethylstilbene. Other unsubstituted azines decompose similarly. Thus the reaction of the decomposition of nuclear azines appears general, and gives a frequently very satisfactory yield of ethylenic compounds. Substituted azines give comparable results, substituted stilbene derivatives being formed.

**Komppa's Synthesis of Camphoric Acid.**—J. F. Thorpe and G. Blanc.—When very dilute alkalis act on the methyl-diketoapocamphorate of methyl the latter is converted into a salt of diketoapocamphoric acid. On acidifying the liquid  $CO_2$  is evolved and a monobasic acid is formed, which when heated gives up more  $CO_2$ , giving the diketone—



The lower homologue of the diketone is prepared by distilling diketoapocamphoric ether with dilute sulphuric acid. These two diketones are characterised by the formation of osazones and dioximes. Thus it appears that in the action of very dilute alkalis on methyl-diketoapocamphoric ether, which conditions are practically realised in Komppa's synthesis of camphoric acid, the  $CH_3$  group remains attached to the carbon.

**Influence of Temperature upon the Activity of Emulsin.**—Gabriel Bertrand and Arthur Compton.—In the diastatic preparation obtained from almonds there are two different diastases:—(1) Amygdalinase, which, if it were present alone, would split the glucoside into phenylglycolic nitrile and amygdalose, and (2) amygdalase, the hydrolysing action of which is limited to amygdalose. The two diastases behave similarly under the action of heat. They exhibit an optimum temperature, which is higher the shorter the duration of the experiment. Thus the optimum temperature is not a constant, and can only be used to characterise certain diastases when the experimental conditions are exactly comparable.

**Oils Extracted from Fruits of Oil Palm.**—Alexandre Hébert.—The author has examined the fruits of six different varieties of *Elaeis nigrescens* and two of *Elaeis virescens*. The yields of oil from the pulp vary from 41–63 per cent, and from the whole fruit from 16–56 per

cent. The constants of the fatty matter which may be extracted from the different varieties are given in detail in the paper.

*Atti della Reale Accademia dei Lincei.*  
Vol. xx., No. 11, 1911.

**New Form of Dilatometer.**—Filippo Boltazzi and G. Buglia.—The authors describe a new form of dilatometer in which two liquids (*e.g.*, a solution or suspension of protein and a reagent) can be made to mix when they have reached a given temperature, without any necessity for handling the apparatus. It consists essentially of two receptacles communicating with one another, in which the two liquids are placed; communication is cut off by a plug of some substance which does not fuse until the required temperature is reached, and which is not dissolved by the liquids.

**Line Spectrum of Nitrogen in Geissler Tubes.**—C. Porlezza.—This paper contains measurements of the line spectrum of nitrogen in the blue and ultraviolet regions, and the author has now completely mapped the line spectrum of nitrogen in Geissler tubes.

**Thermic Analysis of Binary Mixtures or Chlorides of Bivalent Elements.**—Carlo Sandonini.—Strontium chloride gives eutectics with the chlorides of cadmium and manganese, and mixed crystals in all proportions with the chlorides of barium and lead. Barium chloride gives a single eutectic with cadmium chloride, and mixed crystals in all proportions with lead chloride.

**Asymmetrical Selenites.**—L. Marino and V. Squintani.—When selenious anhydride acts on piperidine a new compound of formula  $C_5H_{10}NH.SeO_2$  is obtained in the form of colourless crystals of melting-point  $70-71^\circ$ . When it is boiled with alkali piperidine distils off. The aqueous and alcoholic solutions give all the reactions of selenious acid. A methyl alcohol solution of the compound gives a white precipitate with an alcoholic solution of zinc chloride; this precipitate consists of zinc selenite,  $ZnSeO_3$ . With platinum chloride a compound of formula  $(C_5H_{11}N.HCl)_2PtCl_4$  is obtained.

## MISCELLANEOUS.

**Royal Institution.**—A General Meeting of the Members of the Royal Institution was held on the 5th inst.; Sir James Crichton-Browne, Treasurer and Vice-President, in the Chair. Mr. E. B. Badcock, the Rev. Prebendary Jeakes, and Mrs. G. Stibbard were elected Members. The Special Thanks of the Members were returned to Mr. G. H. Griffin for his Donation of £21 to the Fund for the Promotion of Experimental Research at Low Temperatures. The Chairman reported that a further sum of £300, part of the legacy of the late Miss Wolfe to the Royal Institution, had been received.

**Literary Note.**—Messrs. Constable and Company will commence the publication in April next of a new quarterly Scientific Review to be entitled "Bedrock, a Quarterly Review of Scientific Thought." The Review will appear as an organ devoted to the full discussion of such subjects as the effect on the race of native and foreign disease, of intemperance, of city life and luxury; the fitness of women for Government; the real nature of the Psychological and Physiological difference between sexes, races, and classes; the present relation of science to religion; theories of evolution and heredity; the trend of scientific and mechanical research, invention, and development—in fact with all the greater problems of modern science in a manner both fundamentally scientific, and, the editors hope, also generally interesting to an educated public. It will further make a feature of notes on current research work and reviews of scientific books. The Editorial Committee consists of Sir Bryan Donkin, F.R.C.P.; Prof. E. B. Poulton,

F.R.S., LL.D., Hope Professor of Zoology in the University of Oxford; Prof. H. H. Turner, D.Sc., F.R.S., Savilian Professor of Astronomy in the University of Oxford; and G. Archdall Reid, F.R.S.E. The acting editor will be Mr. H. B. Grylls.

**City and Guilds of London Institute.**—At a Meeting of the Council of the City and Guilds of London Institute held on Monday, January 29th, 1912, the Fellowship of the Institute was conferred upon Mr. Noel Deerr and Mr. Leonard P. Wilson. This distinction is conferred upon those students who having obtained the Associateship and spent at least five years in actual practice, produce evidence of having done original and valuable research work or of having otherwise contributed to the advancement of the industry in which they are engaged. Since Mr. Noel Deerr gained his diploma of Associate at the close of his course of study at the City and Guilds (Engineering) College in 1896 he has been occupied as chemist to cane-sugar factories in British Guiana, Mauritius, and Honolulu; he has rendered signal services to the cane-sugar industry by his original work and by the publication of a comprehensive book on cane-sugar dealing with both the agricultural and manufacturing side of the industry. Mr. Leonard P. Wilson gained his diploma in 1899, and subsequently held the Leathersellers' Company's Research Fellowship. He is at present one of the chemists at the artificial silk works of Messrs. Courtauld and Company at Coventry. His work in connection with the artificial silk industry has been of special value, and his inventions are embodied in several patents taken out in his name conjointly with that of his firm.

## MEETINGS FOR THE WEEK.

- MONDAY, 12th.—Royal Society of Arts, 8. (Cantor Lecture). "The Meat Industry," by Loudon M. Douglas, F.R.S.E.  
TUESDAY, 13th.—Royal Institution, 3. "The Study of Genetics," by Prof. W. Bateson, F.R.S.  
— Society of Dyers and Colourists, 8. "New Apparatus for the Control of Water Purification and like Purposes," by Hon. R. C. Parsons. "Water Treatment by means of the Permutit Process," by L. H. Harrison and S. Rideal.  
WEDNESDAY, 14th.—Royal Society of Arts, 8. "Gem Engraving," by Cecil Thomas.  
THURSDAY, 15th.—Royal Institution, 3. "The Portraiture of Shakespeare," by M. H. Spielmann, F.S.A.  
— Royal Society. "Specific Instance of the Transmission of Acquired Characters—Investigation and Criticism," by T. G. Brown. "Experiments on the Cross-breeding of Two Races of the Moth, *Acidalia virgulana*," by W. B. Alexander. "Effects of Castration and Ovariectomy upon Sheep," by F. H. A. Marshall. "Causes and Prevention of Miners' Nystagmus," by T. L. Llewellyn. "The Stomatograph," by W. L. Balls. "Composition of the Blood Gases during the Respiration of Oxygen," by G. A. Buckmaster and J. A. Gardner.  
— Chemical, 8.30. "Chemical Examination of Scammony Root and of Scammony," by F. B. Power and H. Rogerson. "Experiments on the Walden Inversion—Part VIII.,  $\alpha$ -Amino- $\alpha$ -phenylpropionic Acids," by A. McKenzie and G. W. Clough. "Preparation of the Nitrites of the Primary, Secondary, and Tertiary Amines by the Distillation and Sublimation in a Vacuum of Concentrated Solutions of Mixtures of the Hydrochlorides of the Bases and Alkali Nitrites," by P. Neogi. "Nitrites of the Mercurialkyl- and Mercurialkyl-lylammonium Series," by P. C. Ray, J. N. Rakshit, and R. L. Datta. "Nitrites of the Alkylammonium Series—Part IV., Isobutylammonium Nitrite, Diethylammonium Nitrite, Dipropylammonium Nitrite, and Tripropylammonium Nitrite, and their Decomposition and Sublimation by Heat," by P. C. Ray and J. N. Rakshit. "Perhalides of Diphenyliodonium Iodide," by M. O. Forster and J. H. Schaeppi.  
FRIDAY, 16th.—Royal Institution, 9. "The Road—Past, Present, and Future," by The Rt. Hon. Sir John H. A. Macdonald, K.C.B., F.R.S., &c.  
SATURDAY, 17th.—Royal Institution, 3. "Franz Liszt (Centenary)," by Sir Alexander C. Mackenzie, Mus. Doc., &c.

ERRATUM.—In Mr. Shelton's letter at p. 60, line 4 from end, "honour of the men of" should read "honour of men of."



# THE CHEMICAL NEWS.

VOL. CV., No. 2725.

## BICENTENARY ANNIVERSARY OF M. V. LOMONOSOFF'S BIRTHDAY.

By B. N. MENSCHUTKIN.

I HAVE little doubt that the name of Mihailo Vasilievic Lomonosoff is quite unknown to English scientists; and yet his work in chemistry and physics is important enough. Since 1902 it has been the object of my investigations, which include both his printed papers and many manuscript notes preserved in the archives of the Russian Academy of Sciences; indeed, considering the fact that since Lomonosoff's death, the buildings of the Academy have been several times destroyed by fire, it is surprising how many of his MSS. came down to us. As on the 8th of November (all dates are given in O.S.), we celebrate the bicentenary of his birthday, a short account of his life and scientific work will, I hope, be acceptable to the readers of this journal.

### I.

The life of Lomonosoff is full of romance. His father was a well-to-do pomor, as are called in the North of Russia people gaining their livelihood from the sea; a simple, illiterate peasant, energetic and clever, possessing some land and several schooners, living on the island Kuróstroff of the North Dvina, opposite the town Holmogori (about thirty miles S.E. from Arhángelsk). Mihailo Vasilievic Lomonosoff was born here on November 8th, 1711, as first child. As the boy reached ten years of age his father began to take him during the short summer of the North to the sea, hoping to make him his successor in business. But the natural phenomena of the North Seas appealed to Michael more than fishing and trade, and he observed with the greatest interest the frequent aurora borealis, the winds, the tides, and the waves, the ice conditions, &c. To study the exact sciences, which would allow him to understand all these natural phenomena, became his dearest wish.

In the late autumn, winter, and spring, when the ice-bound waters permitted no navigation, Lomonosoff could devote some of his time to learning. Having quickly mastered reading and writing from the only books that he could get at first—church books—he soon became an expert reader of them in church. He knew that to learn the exact sciences a knowledge of Latin was indispensable, as almost all the scientific literature at the beginning of the eighteenth century was written in that language; Holmogori had a Latin school (founded in 1723), but it was impossible for Lomonosoff to enter it; at that time and for many years afterwards *the peasants were forbidden by law to visit the schools*. Nothing was left to him but to gather such knowledge as he could from stray books that fell into his hands from the shipbuilding yards about Holmogori and from sailors and traders.

After the death both of his mother and the first stepmother his father married a third time (1724); the second stepmother took a violent dislike to Michael, and continually scolded him for wishing to read books and be wiser than his parents. It is hardly a matter of wonder that after some years of such life Lomonosoff resolved to abandon his native home and go to Moscow, with which a brisk trade was carried in those days by Arhángelsk and Holmogori.

This resolve Lomonosoff put into practice in December, 1730, having, with the consent of his father—who certainly dearly loved his only son—got a passport allowing him to absent himself for one year. The journey to the capital, performed on foot, took several weeks, and it was the end

of January, 1731, when he succeeded at last in becoming a student of the only higher institute of learning that Moscow possessed at the time—the Academy of Divinity—having told everybody that he was the son of a nobleman of Holmogori. In the autumn of that year, as he did not return to his native village, he was proclaimed there a runaway peasant.

The life of Lomonosoff in Moscow must have been one continuous hardship. Imagine a young man of twenty, high of stature, with a big voice, doing schoolwork together with boys of ten or twelve, who laughed at him and his manners; this same young man receiving an allowance of three kopeks (three farthings, equal to about 9d. of to-day) per diem, wherewith to obtain the daily bread and all other necessities, knowing full well at the same time that should he choose to return home he could immediately take a wife with a rich dowry, and live comfortably on the proceeds of his father's trade.

All this did not deter Lomonosoff from studying with all his might, and he passed three classes during the first year. He soon mastered the Latin language, and could speak it fluently; but as he proceeded from class to class he saw with dismay that his wish could not be fulfilled, neither exact nor natural sciences were taught in the Academy of Divinity. In 1734 he was obliged by force of circumstances to acknowledge himself to be a peasant, with no right to be in the Academy at all, and it was doubtless only the fact of his being the best scholar that prevented his expulsion. The outlook was indeed a gloomy one; as a peasant he could not even become a priest. We do not know what plans he had for the future, when there happened quite unexpectedly a series of unusual events, which altered completely this state of affairs.

In 1720 Peter the Great founded at St. Petersburg the Russian Academy of Sciences, incorporated with a University College, and the Academicians were at the same time professors giving courses of lectures to the students. In 1735, as there were very few students in Petersburg—the town itself was founded only in 1703—the Senate gave an order to the Academy of Divinity in Moscow to send twenty of their best scholars to the University. This order was promptly executed, but only twelve students of the ultimate and penultimate classes were fit to be sent; needless to say that among them was Lomonosoff. They arrived at St. Petersburg on January 2nd, 1736, and became students of the University.

At that time a great expedition, sent by the Academy of Sciences in 1733, was exploring Siberia—then a land almost unknown. This expedition was in need of a chemist acquainted with mining and metallurgy; as no such man was to be found the Academy decided to send three students to Germany—there to study chemistry, mining, and metallurgy. One of them happened to be Lomonosoff; thus all his wishes were fulfilled in an unexpected manner, certainly surpassing his wildest dreams.

November, 1736, saw our students already in Marburg, beginning to learn the German language and the necessary exact sciences—mathematics, physics, chemistry, mechanics; their course of studies embraced also philosophy, French, and drawing, all under the supervision of the celebrated philosopher, Prof. Baron Christian Wolff, who was also a member of the Russian Academy. During their stay in Marburg the students received a liberal allowance—300 roubles yearly (equal to about £250 of modern money); but the transition from the utmost poverty and the severe restraint of the Academy of Divinity to the full liberty of the German student's life was too much for them; they plunged recklessly into their new life without thinking of the consequences. The result was that when their stay at Marburg came to an end (July, 1739), it was discovered that they not only had spent all their allowance, but had contracted debts to the equivalent of £10,000 of modern money! Prof. Wolff had to cover these debts out of his own pocket, pending the arrival of this sum from the Academy of St. Petersburg. In spite of all this Wolff recognised the great abilities of

Lomonosoff, and was satisfied that the latter would prove a man of genius.

After Marburg the three students repaired to Freiberg in Saxony, where Bergrath J. F. Henckel—at that time one of the leading German metallurgists—undertook to teach them mining and metallurgy. He was charged also by the Academy with the money matters of our students, whose allowance was now greatly reduced in order to cover the debts contracted at Marburg—an arrangement that was very distasteful to them, and caused much ill-feeling. After several violent conflicts with Henckel, Lomonosoff left Freiberg in May, 1740, with the intention of putting his case before the Russian Ambassador to Saxony, but did not find him at Leipzig, and returned to Marburg, where he married in June Elizabeth Zilch, the daughter of a church dignitary.

But the married couple could not long enjoy their bliss; there was the stern question of what to do next. Lomonosoff thought it best to return to Russia by way of Amsterdam, which was then the chief centre of Russian trade. On arriving there he found some acquaintances, who advised him not to return without an order from the Academy; he accordingly decided to retrace his steps to Marburg. On his way back he was caught by a Prussian recruiting officer and forced to enlist in a Hussar regiment, whose quarters were in the fortress of Wesel. Lomonosoff succeeded after several weeks in escaping from this fortress, and after hairbreadth escapes came back to his wife in Marburg, where he lived through the winter.

In May, 1741, according to the instructions received from the Academy, he alone sailed from Lübeck and landed on the 8th of June in Petersburg; his wife joined him several years later. A strange thing happened to Lomonosoff during this voyage; he saw in a dream his father lying dead on a desert island of the White Sea, which they had often visited together. On his arrival at St. Petersburg he hastened to the tavern frequented by traders from Holmogori, found there some of them and persuaded them to explore on their return this island. They did it, with the result that they found there the corpse of Lomonosoff's father and buried him.

On his return Lomonosoff presented to the Academy specimens of his knowledge—some physical dissertations—and was made in January, 1742, adjunct in physics of the Academy, with a salary of 360 roubles. At that time he began to compose odes on festive occasions, such as the birthdays and namesdays of the sovereign; as he employed new (metric) forms in Russian poetry and created the literary Russian language, these odes surpassed anything written before by their powerful and sonorous language, and were greatly appreciated at Court; thus he soon became famous as a poet, and received several times costly presents from the reigning sovereigns. His philological work on the Russian language and its grammar is of the greatest value.

After the death of Peter the Great the ruling monarchs changed in rapid succession. Under the reign of Anna Ivanovna the direction of all the affairs fell into the hands of Germans, this state of things culminating in the regency of Biron. Everybody began to hate the Germans; a natural reaction made itself felt, and on the 25th of November, by a *coup d'état*, the throne was occupied by Elisabeth, daughter of Peter the Great. The Russian Academy of Sciences, which at that time did not contain a single Russian, also felt the repercussion of these events: grave accusations were brought forward against J. Schumacher, librarian and secretary of the Academy, who managed to get control of all the money affairs. Lomonosoff did not take part in these accusations, but, often in liquor, fought some battles with his German neighbours, and showed open defiance of the academicians, with the result that he had to spend eight months in 1743 under arrest in very straitened circumstances. There was at that time no money in the Academy, and the salary was paid in books, which the recipient could sell to whom he pleased for what they would fetch. Only in January, 1744, was he set free;

as a further punishment he had to beg pardon of the assembled academicians, and his salary was reduced by half for six months.

It seems that the forced retirement occasioned by the arrest had a beneficial influence. Lomonosoff studied hard during that time, and wrote, in 1744, several important papers (about which I will presently say), which were communicated to the academicians and printed afterwards in the *Commentarii* of the Academy. In 1745, having presented a dissertation on the tincture of metals, he was made academician and professor of chemistry (the first Russian academician). In this capacity he built in 1748, having overcome many obstacles, a chemical laboratory, the first in Russia where scientific experiments were made and students taught. In this laboratory he worked a great deal during the following years. Having seen some Roman mosaics Lomonosoff conceived the idea of making mosaics out of pieces of coloured glass. After several thousands of experiments he could produce opaque glass of any colour, and in 1752 made the first picture, which was presented to the Empress and much admired. In 1753 he received from the Crown an estate, not far from Petersburg, containing some 40,000 acres, several villages with 211 souls (211 male inhabitants), in order to build glassworks and have sufficient hands for them; thus a former peasant had now himself an enormous estate and hundreds of serfs under him. Afterwards a great mosaic studio was erected by Lomonosoff in Petersburg. His best production, very effective and bright of colour, is an enormous mosaic picture (21 feet long, 15 feet high), representing the battle of Poltava, finished in 1764, and preserved now in one of the museums of Petersburg.

Many experiments of scientific interest were also made in the chemical laboratory; I will describe them in the second part of this paper. Lomonosoff worked here till 1757, when he gave over the professorship of chemistry to Salchow, and busied himself with other branches of natural sciences—geology and mineralogy being the principal among them. The last years of his life were devoted to Russian history, to geographical problems (he organised expeditions to the North Seas), to the study of ice formation in the ocean, to an investigation of the force of gravitation through pendulums, to the invention of new instruments for accurate determination of latitude and longitude at sea. Even in astronomy this universal genius made some important work; for instance, in May, 1761, whilst observing the passage of Venus across the sun's disc he discovered that the planet Venus had a great atmosphere, a discovery usually attributed to Schröter and Herschel, who made it thirty years after Lomonosoff.

In concluding this part I must dwell also on another side of Lomonosoff's activity. Knowing by bitter experience the awful conditions of life of the peasants, he tried in all possible ways to better their lot, to make them happier, to give them knowledge they needed so much. We find these sentiments expressed in his poems and odes, where his ideal of a just, gracious monarch is often given; in his remarkable letter on the conservation and multiplication of Russian people, and many other writings. He created the Russian scientific language in his translations and scientific allusions held in the Academy; he was the first to hold public lectures on physics in Russia; to him is due the foundation of the University of Moscow in 1755, and until his death he was the head of the University and Gymnasium at St. Petersburg.

I have tried in these few words to present the life history of a peasant who was certainly one of the greatest men of his epoch. Lomonosoff was well received by many important noblemen of his time, and often received valuable help from some of them. His scientific work gained him honourable membership of the Academies of Sciences of Stockholm and Bologna; he received many other distinctions and titles. He himself, although a man of simple habits, was perfectly aware of his importance, and always stood up for his dignity; many were the collisions with different persons brought about by his somewhat choleric



temper. The last years of his life he was often ill—a consequence of intemperance, the besetting sin of Russians of all times—and died at St. Petersburg on April 4th, 1765.

(To be continued).

# SMALL ELECTRIC FURNACE WITH HEATING ELEMENT OF DUCTILE TUNGSTEN OR DUCTILE MOLYBDENUM.\*

By R. WINNE and C. DANTSIZEN.

THERE are many uses for a simple furnace which can be run higher than the melting-point of iron, and in which substances can be heated without taking up either carbon or oxygen.

There have been a few special furnaces, electrically heated, which are capable of fulfilling these conditions. Of these we may mention the following:—

1. The iridium-tube furnace. This is very fragile and extremely expensive.

2. A carbon-tube furnace with a porcelain tube inside. This makes an excellent tube-furnace, but calls for special transformers.

3. The platinum foil or wire-bound body of a fire-clay or other refractory. This has been to the average man the most easily accessible and most generally used form of small furnaces for fulfilling the conditions. But it has its limitations. Most serious of these are the fact that the platinum is easily contaminated, and that, except for small sizes, the winding is very expensive. Besides this, much of the work for which these furnaces are used necessitates running the platinum perilously close to its melting-point.

4. The Arsem vacuum furnace (*Trans. Am. Electrochemical Soc.*, 1906, ix., 153; *Journ. Am. Chem. Soc.*, xxviii., 921), in which a graphite heater is used to generate

denum. It is wound on G, an alundum cylinder which is moulded plain inside and with a helical groove on its outer surface. A is a Battersea crucible. B is an inverted Battersea of which the bottom has been cut off. C is the crucible bottom, used as a cover. The bottom of A, as well as the space between A and B, is filled with powdered silica.

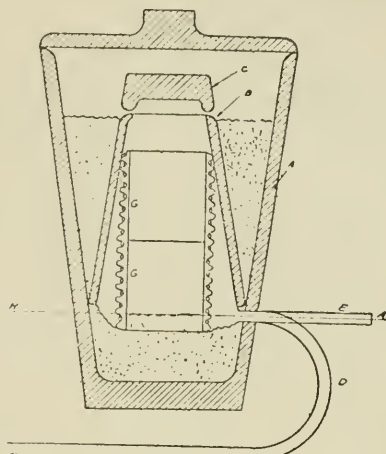


Fig. 1.

Hydrogen is constantly supplied to the furnace through the pipe D, and burns as it escapes from the top of B. This gives a protecting atmosphere for both the tungsten or molybdenum winding and the object to be heated. Current is supplied to the winding through two large copper connectors, E E.

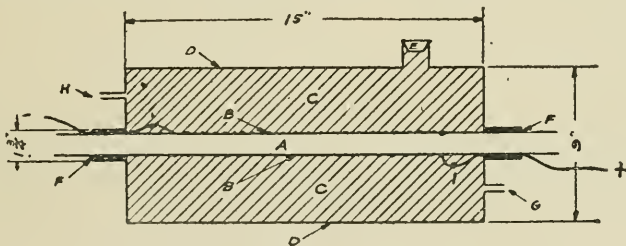


Fig. 2.

the heat, and in which the oxidation is prevented by the vacuum. This introduces carbon when very high temperatures are used.

We will show in the following how two simple types of furnaces have been made with a winding of ductile tungsten or molybdenum. It is now possible to produce these substances in the form of wire or ribbon, and their high melting-points and relatively low cost adapt them admirably to the purpose.

## Crucible Furnace.

This consists of a helix of ductile tungsten or molybdenum, supported by an alundum tube and protected from oxidation by a hydrogen atmosphere. The container, for the charge to be heated, is a small crucible which is placed inside of the alundum cylinder.

The diagram, Fig. 1, shows the furnace in vertical section. W is the heating wire, of ductile tungsten or molyb-

An object to be merely heated, as for annealing, may be inserted directly into the alundum cylinder.

Material to be melted is placed in a small crucible, and this is let down into the alundum cylinder. An especially nice crucible to hold the charge is made of pure alumina.

A few dimensions and details of construction may be of interest.

In the apparatus shown in Fig. 1, the Battersea crucibles A and B are sizes O and J respectively. The alundum body G consists of two cylinders placed end to end. Each is 7.6 cm. high and 5.1 cm. inside diameter, while the distance from one convolution of the helix to the next is 0.95 cm. These alundum cylinders may be obtained from the Norton Company, of Worcester, Mass. The winding consists of 260 cm. of square molybdenum wire, 1.27 mm. on a side. This wire is first wound on a mandrel 3.8 cm. in diameter, and wire and mandrel are then heated up to about 800° C. Upon then releasing the coil it expands to the diameter of the alundum body, on which it can then be screwed. The copper connectors, E E, are 0.8 cm. in diameter, and the ends of the coil are simply clamped in

\* Paper prepared for the Twentieth General Meeting of the American Electrochemical Society. From the *Chemical Engineer*, xlv., No. 5.

with set-screws. The copper connectors and the hydrogen inlet tube are held in place in the crucible wall to a mixture of powdered silica and water glass, which at the same time prevents loss of hydrogen.

This furnace can be safely run up to 1700° C. At this temperature it calls for 25 volts and 45 amperes.

We have melted pure iron and made many iron and other alloys in this furnace.

#### *Tube Furnace.*

This consists of a porcelain or alundum tube, wound with tungsten or molybdenum foil. Around the tube is a tight metal casing filled with powdered silica, and, to prevent oxidation of the winding, a hydrogen atmosphere is maintained in the casing.

Such a furnace is shown in the diagram, Fig. 2, in vertical length section. A is an alundum tube, 2.2 cm. inside diameter and 46 cm. long. The casing D is made of thin sheet iron and is oxyacetylene welded. The winding is a molybdenum ribbon, 0.184 mm. thick, 2.54 mm. wide, and 445 cm. long. I I are heavy copper leads, fastened to the ends of the coil by twisting the latter about them. C is the powdered silica packing; F F is some asbestos wool, used to prevent the escape of hydrogen at the ends of the casing. H and G are hydrogen inlet and outlet tubes respectively. E is a rubber stopper.

At this temperature it calls for 80 volts and 14.3 amperes.

The two furnaces above described are adapted to heating the charge in an atmosphere of hydrogen. In case it were desirable to heat in an oxidising atmosphere, it would be necessary to replace the very porous alundum by porcelain, as otherwise the furnace winding would become oxidised.

### THE USE OF SULPHUR MONOCHLORIDE IN THE DETERMINATION AND ANALYSIS OF THE RARE EARTH MINERALS.\*

By WILLIAM BROOKS HICKS.

(Concluded from p. 64).

For the analysis of eschynite some pure crystals, as free as possible from foreign matter, were ground to a fine powder, and then subjected to the action of sulphur monochloride. As the decomposition proceeded, the volatile chlorides and the excess of sulphur monochloride passed into a dilute nitric acid solution and were there decomposed. Much of the sulphur was oxidised, and consequently less free sulphur was precipitated. At the end of the operation dry hydrochloric acid gas was passed through the combustion tube, and, by means of a free flame, all the volatile portion was driven out. After cooling in a current of hydrochloric acid gas the tube was cut by scratching with a file and touching with a hot glass rod. The short end of the tube and the glass cover were thoroughly washed into the beaker, which now contained all the columbium, tantalum, titanium, tungsten, and most of the iron from the mineral, as well as a considerable amount of separated sulphur. This mixture was treated as follows:—

The lumps of sulphur were broken up as much as possible by means of a glass rod, a large excess of ammonium hydroxide was added, and then hydrogen sulphide in sufficient quantity to dissolve the sulphur completely. The yellow ammonium sulphide thus formed dissolved the tungstic acid, leaving the acid earths and iron in the residue. This was filtered off. By acidifying the filtrate, tungsten sulphide was precipitated along with a large amount of

sulphur. After filtering, the precipitate was washed with water, alcohol, and carbon disulphide. The precipitate was then evaporated with nitric acid, ignited, and weighed as  $\text{WO}_3$ .

The residue, containing iron and the acid earths, was digested with hot, dilute sulphuric acid until perfectly white. All the iron and some of the acid earths went into solution, which was decanted through a filter and the residue washed. Hydrogen sulphide was passed into the filtrate to reduce the iron, and then sodium carbonate was added until the solution became almost neutral. This solution was boiled for an hour, during which time a current of hydrogen sulphide was passed through the solution to prevent the oxidation of the iron. By this means the acid earths were completely precipitated, while the iron was left in solution. This precipitate was added to that obtained above, ignited, and weighed. No attempt was made to separate columbium, tantalum, and titanium.

The non-volatile portion was dissolved in water, to which a few drops of hydrochloric acid had been added. The solution was boiled and filtered from the gang. The filtrate was treated with hydrogen sulphide to remove the lead and tin. These were separated in the usual way. The filtrate, after removing the lead and tin, was treated with an excess of ammonium chloride and ammonium hydroxide. All the iron and rare earths were precipitated. Calcium was determined in the filtrate. The rare earths were separated from the almost negligible amount of iron by ammonium carbonate and ammonium sulphide.

By an application of this method of procedure the following results were obtained:—

|                                                                                                           | Per cent. |
|-----------------------------------------------------------------------------------------------------------|-----------|
| $\text{Cb}_2\text{O}_3$ , $\text{Ta}_2\text{O}_5$ , $\text{TiO}_2$ . . . . .                              | 53.55     |
| $\text{ThO}_2$ , $\text{Ce}_2\text{O}_3$ , $\text{La}_2\text{O}_3$ , $\text{Y}_2\text{O}_3$ , &c. . . . . | 41.30     |
| $\text{WO}_3$ . . . . .                                                                                   | 0.17      |
| $\text{SnO}_2$ . . . . .                                                                                  | 0.04      |
| $\text{FeO}$ . . . . .                                                                                    | 0.82      |
| $\text{CaO}$ . . . . .                                                                                    | 0.55      |
| $\text{PbO}$ . . . . .                                                                                    | 0.91      |
| Gang . . . . .                                                                                            | 0.22      |
| Loss on ignition . . . . .                                                                                | 2.25      |
|                                                                                                           | 99.81     |

The only purpose of this analysis was to show that the sulphur monochloride method of decomposition could be used in the analysis of eschynite. The results obtained above prove this point. Owing to the lack of time neither columbium, tantalum, and titanium, nor the rare earths, were separated, yet it is obvious that any of the methods proposed for separating these elements could readily be applied.

The principal advantages of this method are the readiness with which the mineral is decomposed by sulphur monochloride, the simplicity and cheapness of the apparatus required, and the separation of columbium, tantalum, titanium, and tungsten from the rare earths during the decomposition. The chief disadvantage that has been encountered in applying the method is the treatment of the volatile portion which consists of the excess of sulphur monochloride mixed with the volatile chlorides. This has been successfully dealt with by allowing the mixture to pass into dilute nitric acid, and then removing the precipitated sulphur by adding excess of ammonium hydroxide and hydrogen sulphide.

Since fergusonite, euxenite, and samarskite are completely decomposed by sulphur monochloride, with the separation of columbium, tantalum, titanium, and tungsten from silica and the rare earths, it is evident that this method of decomposition could likewise be used in their analysis. By analogy, we would reason that columbates, tantalates, and titanates in general would be decomposed by sulphur monochloride, and that this method of decomposition would lend itself to their analysis.

\* From the *Journal of the American Chemical Society*, xxxiii., No. 9.



# TECHNICAL UTILISATION OF LITTLE KNOWN METALS.

By Dr. W. R. WHITNEY.

WE may not need special evidence to convince ourselves that we are living in a rapidly improving technical age. The development of our industries testifies clearly on this point. That chemistry has an important part in this development, particularly in our own country, could be guessed from a knowledge of the fact that there are fully ten times as many chemists here as there were twenty years ago. These men are at work on more than ten times as many different materials as were known twenty years ago, and the end is not yet.

An interesting and instructive view of the rate of advance of chemistry in our era may be gained from a study of the known metallic elements.

It is plain that new chemical compounds, in general, are coming into commercial use so rapidly that it is hopeless to even attempt collection of data. It is safe to say that if we include organic compounds, there are many hundreds of new substances made and described each year. Hundreds of these will be useful for years, solely as systematising marks for themselves and for other compounds, but in this way a very strong foundation is being built for the future of chemistry. Any adequate summary for this general field is impracticable because of its magnitude.

In case of the chemical elements a survey is more simple, and particularly with the metallic elements. The metallic elements have a special interest in this connection, because they are limited in number, their properties are known, and some of them have been used for ages. A philosopher would probably maintain that as our wants become more and more differentiated, we will call into use more and more of this store of metals. This is practically what has been done in the past. That we still have no considerable use for metallic barium, for example, is explained by an insufficiently developed requirement. More easily obtainable metals have thus far fulfilled needs which will finally grow so complex as to require metallic barium.

But this rate of increase in demand for new metals to fill new wants has not been a constant one—far from it. It never was nearly so rapid as at present, and it characterises our technical age. We have in all about fifty elementary substances which we can call metals or metalloids. Not more than a very few others seem probable of discovery. We want to point out the rate of increase of use, to what we may call an appreciable extent, of these metals in their metallic state. This excludes from consideration uses of compounds or salts of the metals.

Of the fifty there were seven which were known and used commercially over two thousand years ago. These are iron, copper, tin, gold, silver, mercury, and lead. There are eight others which were introduced into practical use more or less extensively between the first and nineteenth century. They are zinc, iridium, platinum, cobalt, nickel, antimony, cadmium, and bismuth; that is, the rate of addition has been less than one metal for each two centuries prior to our century. Within our own time, say about a quarter century, there have been about fourteen more metals added to commercial use, or a rate more than one hundred-fold greater than the previous rate.

These values may be modified somewhat by use of different criteria of commercial use, but the conclusions remain about the same.

We are now rapidly seeing practical use made of a large part of our little group of known metals. Those which have been introduced into commercial use during the past quarter century, either pure or intentionally alloyed, are aluminium, magnesium, silicon, cerium, vanadium, tungsten, tantalum, osmium, chromium, selenium, molybdenum, titanium, boron, and manganese. The rate of

addition must soon rapidly fall off, but among those which seem to call for some attention and demand introduction is calcium. Its common occurrence promises a long and useful life; but thus far, its peculiar properties have not suited specific requirements. It will be interesting to watch its development. Can it possibly go through any such varied and complex series as iron has experienced, for example? At one time there was only a single kind of iron. It met the needs of the time. Later, we find the uses distributed over what was called cast-iron, wrought-iron, and steel. Then several entirely different cast-irons and wrought-irons appeared, each of which filled some particular use. Among the steels there are already a myriad of varieties. The carbon steels, which, for a long period of time, were the only steels, are now overshadowed by the special alloy steels, and it seems as though there would be no end to this development. Nickel steels find use in armour plate. Tungsten and chromium steel is the leader in high-speed cutting tools. Molybdenum steel makes most useful permanent magnets for electric meters. Silicon steel fits best the demands of electric transformers, because of its low magnetic hysteresis and high resistivity. Titanium steel is said to be superior for railroad rails. Vanadium steel is apparently particularly valuable for springs, and thus the list grows. All of these alloy steels are the product of the last quarter century, and it is perfectly evident that with the introduction of electric furnaces, the special steel alloys are bound to be still further developed.—*Journal of Industrial and Engineering Chemistry*, iii., No. 7.

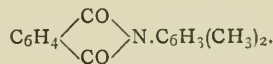
## ISOMERIC PHENYLPHTHALIMIDES AND SOME ALLIED COMPOUNDS.\*

II.

By MITSURU KUHARA and SHIGERU KOMATSU.

(Concluded from p. 63).

16. s-Paraxylylphthalimide,—

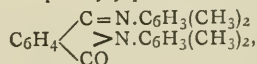


This substance was prepared by the action of paraxylidine upon phthalyl chloride or phthalic anhydride, as in the case of orthoxylidine. It crystallises in fine needles from its alcoholic solution and melts at 147–148°. It is soluble in alcohol, benzene, and chloroform. The analysis gave the results here given:—

- I. 0.2055 grm. of the substance gave 0.5706 grm. CO<sub>2</sub> and 0.1055 grm. H<sub>2</sub>O.
- II. 0.3612 grm. of the substance gave 1.014 grm. CO<sub>2</sub> and 0.1903 grm. H<sub>2</sub>O.
- III. 0.1574 grm. of the substance gave 7.4 cc. N (15°, 759 mm.).

|             | Calculated for<br>C <sub>6</sub> H <sub>4</sub> (CO) <sub>2</sub> N.C <sub>6</sub> H <sub>3</sub> (CH <sub>3</sub> ) <sub>2</sub> . | Found. |       |      |
|-------------|-------------------------------------------------------------------------------------------------------------------------------------|--------|-------|------|
|             |                                                                                                                                     | I.     | II.   | III. |
| Carbon ..   | 76.50                                                                                                                               | 75.92  | 76.68 | —    |
| Hydrogen .  | 5.18                                                                                                                                | 5.72   | 5.84  | —    |
| Oxygen ..   | 12.78                                                                                                                               | —      | —     | —    |
| Nitrogen .. | 5.58                                                                                                                                | —      | —     | 5.51 |

17. Di-paraxylylphthalidiimide,—



This compound is formed from di-paraxylylphthalamide. It crystallises from alcohol in yellow plates, and melts at 133–134°. It is soluble in ether, alcohol, benzene, and

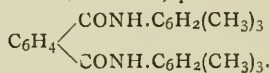
\* *Memoirs of the College of Science and Engineering, Kyoto Imperial University*, ii., No. 12.

chloroform. The substance was analysed, and its nitrogen determined.—

0.2 grm. of the substance gave 12 cc. N (13°, 755 mm.).

|                | Calculated for<br>$\begin{matrix} \text{C}=\text{N.C}_6\text{H}_2(\text{CH}_3)_2 \\ >\text{N.C}_6\text{H}_2(\text{CH}_3)_2. \end{matrix}$ | Found. |
|----------------|-------------------------------------------------------------------------------------------------------------------------------------------|--------|
|                |                                                                                                                                           |        |
| Nitrogen .. .. | 7.91                                                                                                                                      | 7.03   |

18. Di-pseudocumylphthalamide,—

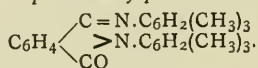


This substance was formed from pseudocumidine and phthalyl chloride, together with normal pseudocumylphthalamide (*Ber.*, xvii., 1802) and isomeric *a*-pseudocumylphthalamide. It crystallises in silky needles from hot alcohol, and melts at 210–212°. It is insoluble in ether, slightly soluble in alcohol, and readily in chloroform. Its analysis gave the following results—

- I. 0.1972 grm. of the substance gave 0.559 grm. CO<sub>2</sub> and 0.133 grm. H<sub>2</sub>O.  
II. 0.1992 grm. of the substance gave 12 cc. N (17°, 759 mm.).

|                | Calculated for<br>$\begin{matrix} \text{C}=\text{N.C}_6\text{H}_2(\text{CH}_3)_3 \\ \text{CONH.C}_6\text{H}_2(\text{CH}_3)_3. \end{matrix}$ | Found. |      |
|----------------|---------------------------------------------------------------------------------------------------------------------------------------------|--------|------|
|                |                                                                                                                                             | I.     | II.  |
| Carbon .. ..   | 77.97                                                                                                                                       | 77.33  | —    |
| Hydrogen .. .. | 7.00                                                                                                                                        | 7.48   | —    |
| Oxygen .. ..   | 8.03                                                                                                                                        | —      | —    |
| Nitrogen .. .. | 7.00                                                                                                                                        | —      | 6.97 |

19. Di-pseudocumylphthaldiimide,—

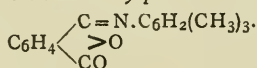


This compound was formed when di-pseudocumylphthalamide was treated with phosphorus pentachloride in dry chloroform. It crystallises in yellow plates from alcohol, and melts at 136–137°. It is soluble in ether, alcohol, benzene, and chloroform. The substance was analysed, and gave the following results:—

- I. 0.2 grm. of the substance gave 0.602 grm. CO<sub>2</sub> and 0.1238 grm. H<sub>2</sub>O.  
II. 0.1233 grm. of the substance gave 7.5 cc. N (15°, 759 mm.).

|                | Calculated for<br>$\begin{matrix} \text{C} < \text{N.C}_6\text{H}_2(\text{CH}_3)_3 \\ = \text{N.C}_6\text{H}_2(\text{CH}_3)_3. \\ \text{CO} \end{matrix}$ | Found. |      |
|----------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------|--------|------|
|                |                                                                                                                                                           | I.     | II.  |
| Carbon .. ..   | 81.67                                                                                                                                                     | 82.09  | —    |
| Hydrogen .. .. | 6.81                                                                                                                                                      | 6.88   | —    |
| Oxygen .. ..   | 4.19                                                                                                                                                      | —      | —    |
| Nitrogen .. .. | 7.33                                                                                                                                                      | —      | 7.10 |

20. *a*-Pseudocumylphthalamide.—

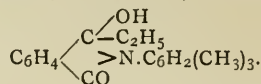


It was formed by the action of pseudocumidine upon phthalyl chloride at a low temperature. It crystallises in yellow needles from the ethereal solution, and melts at 117–118°. It is soluble in ether, alcohol, benzene, and chloroform. Its analysis gave the results here recorded:—

- I. 0.219 grm. of the substance gave 0.621 grm. CO<sub>2</sub> and 0.1172 grm. H<sub>2</sub>O.  
II. 0.2214 grm. of the substance gave 10 cc. N (18°, 762 mm.).

|                | Calculated for<br>$\begin{matrix} \text{C}=\text{N.C}_6\text{H}_2(\text{CH}_3)_3. \\ >\text{O} \end{matrix}$ | Found. |      |
|----------------|--------------------------------------------------------------------------------------------------------------|--------|------|
|                |                                                                                                              | I.     | II.  |
| Carbon .. ..   | 76.98                                                                                                        | 77.35  | —    |
| Hydrogen .. .. | 5.66                                                                                                         | 5.94   | —    |
| Oxygen .. ..   | 12.08                                                                                                        | —      | —    |
| Nitrogen .. .. | 5.28                                                                                                         | —      | 5.33 |

21. 2-Pseudocumyl-3-ethyl-3-oxy-isindolinone,—



By the action of magnesium ethyl iodide on normal pseudocumylphthalamide or *a*-pseudocumylphthalamide, the same substance or 2-pseudocumyl-3-ethyl-3-oxy-isindolinone was obtained. It is soluble in alcohol and ether, and crystallises in colourless plates, and melts at 152–153°. The analysis of the substance gave the following results:—

- I. 0.123 grm. of the substance gave 0.3537 grm. CO<sub>2</sub> and 0.085 grm. H<sub>2</sub>O.  
II. 0.1561 grm. of the substance gave 6.7 cc. N (16°, 759.7 mm.).

|                | Calculated for<br>$\begin{matrix} \text{C} \begin{matrix} \text{OH} \\ \text{C}_2\text{H}_5 \end{matrix} \\ >\text{N.C}_6\text{H}_2(\text{CH}_3)_3. \\ \text{CO} \end{matrix}$ | Found. |      |
|----------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------|------|
|                |                                                                                                                                                                                | I.     | II.  |
| Carbon .. ..   | 77.29                                                                                                                                                                          | 78.36  | —    |
| Hydrogen .. .. | 7.12                                                                                                                                                                           | 7.59   | —    |
| Oxygen .. ..   | 10.84                                                                                                                                                                          | —      | —    |
| Nitrogen .. .. | 4.75                                                                                                                                                                           | —      | 4.94 |

## CHEMICAL NATURE OF SOIL ORGANIC MATTER.\*

By OSWALD SCHREINER and EDMUND C. SHOREY.

(Concluded from p. 62).

### CONCLUSION.

THE methods by means of which the isolation of the substances from the organic matter of soils was accomplished may be briefly shown in the accompanying schematic representation (Chart A), although for actual working details the text must be consulted.

In the preceding pages, and in an earlier Bulletin, the isolation of twenty organic compounds from soils has been described, and while the compounds isolated from any one soil is, in most cases, but a portion of the soil organic matter, the data obtained are sufficient to warrant certain conclusions regarding this important soil constituent.

In the first place, it is evident that the organic matter of soils is made up of a large number of chemical compounds. This might very well be assumed on theoretical grounds, and it has been pointed out in previous Bulletins (*Bull.* 47 and 53, "Bureau of Soils," U.S. Dept. Agr.) that plants, which constitute the greater portion of the material out of which the organic matter of soils is made, contain a vast number of chemical compounds that are added to the soil on the death and decay of the plants. Now, while there seems to be no disposition to question this fact, there has been the assumption on the part of many agriculturists that in some mysterious way this conglomerate of plant compounds added to the soil becomes transformed by decomposition into a single group of closely related bodies, humic acid, &c., and that no matter how varied may be the organic remains, or how diverse the condition of decay, soils vary in organic matter chiefly in amount. That this is not so is sufficiently proven by the facts here established.

\* Bulletin No. 74, U.S. Department of Agriculture, Bureau of Soils.



CHART A.

| Method of separation.                                                                                                                                                         |                                      |                                   | Class.                       | Compound isolated and identified.   |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------|-----------------------------------|------------------------------|-------------------------------------|
| Humus precipitate .. ..                                                                                                                                                       | Alkaline extract .. ..               | Hot alcohol extract .. ..         |                              |                                     |
| { Soluble in alcohol .. ..                                                                                                                                                    | { Soluble in petroleum ether .. ..   | { Insoluble in cold alcohol .. .. | Acids .. ..                  | $\alpha$ -Hydroxystearic acid.      |
|                                                                                                                                                                               |                                      |                                   | Acids .. ..                  | Paraffinic acid.                    |
|                                                                                                                                                                               |                                      |                                   | Fats .. ..                   | Liquid glycerides.                  |
|                                                                                                                                                                               |                                      |                                   | Resinous bodies .. ..        | Resin acids.<br>Resin esters.       |
| { Insoluble in alcohol.<br>Shaken out by ether .. ..<br>Precipitated by silver nitrate in neutral solution .. ..<br>Precipitated by silver nitrate in alkaline solution .. .. | { Insoluble in petroleum ether .. .. | { Insoluble in cold alcohol .. .. | Acids .. ..                  | Dihydroxystearic acid.              |
|                                                                                                                                                                               |                                      |                                   | Acids .. ..                  | Picolinecarboxylic acid             |
|                                                                                                                                                                               |                                      |                                   | Pyrimidine derivatives .. .. | Cytosine.                           |
|                                                                                                                                                                               |                                      |                                   | Hexone bases .. ..           | { Histidine.<br>Arginine.           |
| { Precipitated by lead acetate in alkaline solution .. ..<br>Precipitated by copper sulphate and sodium bisulphite .. ..                                                      | { Insoluble in petroleum ether .. .. | { Insoluble in cold alcohol .. .. | Pentosan .. ..               | Xylan.                              |
|                                                                                                                                                                               |                                      |                                   | Purine bases .. ..           | { Xanthine.<br>Hypoxanthine.        |
|                                                                                                                                                                               |                                      |                                   | Hydrocarbons .. ..           | Henriacanthene.                     |
|                                                                                                                                                                               |                                      |                                   | Cholesterol compounds .. ..  | { Phytosterol.<br>Agrosterol.       |
| { Soluble in petroleum ether .. ..                                                                                                                                            | { Insoluble in petroleum ether .. .. | { Insoluble in cold alcohol .. .. | Acids .. ..                  | Agroceric acid.<br>Lignoceric acid. |
|                                                                                                                                                                               |                                      |                                   | Resinous bodies .. ..        | Resin acid I.                       |
|                                                                                                                                                                               |                                      |                                   | Resinous bodies .. ..        | Resin acid II.                      |
|                                                                                                                                                                               |                                      |                                   | Resinous bodies .. ..        | Resin acid III.<br>Resin ester.     |

Again, not only is the organic matter of soils made up of a large number of compounds, but these compounds represent a number of distinct chemical groups or classes. In the twenty compounds isolated and described there are nine classes of chemical compounds represented, and when consideration is given the fact that there are many indications of the presence of compounds of other classes where as yet there has been no compound isolated, the conclusion is warranted that the types of compounds in the soil organic matter are quite as varied as in plants or animals. While it is true that the tendency in the decay of organic matter is toward simpler compounds, and ultimately to a few simple compounds or the elements, the material known as soil organic matter is in the transition stage from the complex compounds of living organisms to the simple ultimate products. When the organic matter has decayed to the stage of such simple compounds as ammonia, nitric acid, free nitrogen, or carbon dioxide, it is no longer organic matter, and much of it may escape from the soil altogether.

The fact that the organic matter of the soil is made up of a large number of compounds representing many types throws some light on the difficulties that the early workers on this subject encountered, and explains why such diverse results were obtained. This may best be illustrated by the Chart B.

Probably no one soil contains all the compounds mentioned in the chart, but when two or more occur together in different soils the proportion is generally quite different, and there are, moreover, in all soils many compounds yet unidentified, so that it is no mystery why Mulder and his co-workers, as well as their modern followers, obtained widely different figures for the elementary composition of what they supposed were single compounds.

The complexity of the organic matter shown to exist makes the interpretation of soil phenomena, in the light of its chemical composition, more difficult, and emphasises the need of a thorough understanding of the nature of this material in handling properly the chemical, physical, and biological problems presented by soils. If the soil organic matter were simple in composition, the problems connected therewith would also be simple, and the results obtained easily interpreted. Take for instance a single compound, lignoceric acid, that occurs in many soils in fair amount. It would be a comparatively simple problem to determine in what way this compound affects the physical properties of powdered quartz or other rock when added to it in different proportions, or to determine its effect, if any, on the growth of plants or the bacterial flora of soils, and if it were the only organic compound in a soil come to some conclusion. But it is only one of many compounds, and if the factors were known for each of them separately, the factors are not necessarily additive, and the problems presented would still be far from a solution. This recognition of the complexity in the soil and of its problems is, however, a step in the right direction, for the difficult problems presented could never be solved without a full understanding of this very complexity. In short, the chemical relations between the various ingredients of a soil are so complex, and the relation of these to living plants so much more so, that it is impossible to make agriculture a true science. Progress, then, along this line seems to lie in the determination of predominant or indicating factors, much the same basis that the modern practice of medicine is founded on. It is quite possible for some form of organic matter to be the determining factor in some physical or biological condition, favourable or otherwise, but this can not be determined unless the nature of the organic compounds in the soil are known, and the methods for identifying them worked out. Moreover, knowledge of the chemical identity of the organic compounds in soils gives a scientific explanation for some of the methods of practical agriculture, and affords a foundation for making recommendations with a certainty otherwise impossible. This is well illustrated in the case of dihydroxystearic acid, a compound known in the laboratory to be easily oxidised.

## CHART B.

Extract soil with alkali.

| Alkaline solution, acidify.                                            |                                                                           | Insoluble.                                |
|------------------------------------------------------------------------|---------------------------------------------------------------------------|-------------------------------------------|
| Acid filtrate.                                                         | Precipitate.                                                              | So-called <i>humin</i> and <i>ulmin</i> . |
| So-called <i>crenic</i> and <i>apocrenic</i> acids.                    | So-called <i>humic</i> and <i>ulmic</i> acids.                            | Identity of components unknown.           |
| Compounds isolated from this filtrate and described in this Bulletin:— | Compounds isolated from this precipitate and described in this Bulletin:— |                                           |
| Dihydroxystearic acid (a).                                             | Resin acids.                                                              |                                           |
| Picoline carboxylic acids (a).                                         | Resin esters.                                                             |                                           |
| Xanthine.                                                              | Glycerides.                                                               |                                           |
| Hypoxanthine.                                                          | Paraffinic acid.                                                          |                                           |
| Cytosine.                                                              | Lignoceric acid.                                                          |                                           |
| Histidine.                                                             | Agroceric acid (a).                                                       |                                           |
| Arginine.                                                              | Agrosterol (a).                                                           |                                           |
| Pentosan.                                                              | Phytosterol.                                                              |                                           |

(a) More fully described in *Bulletin* 53, U.S. Department of Agriculture, Bureau of Soils.

## CHART C.

Soil containing 0.955 per cent organic carbon.  
Extracted with 2 per cent sodium hydroxide.

| Insoluble.                                     |  | Alkaline solution.                          |
|------------------------------------------------|--|---------------------------------------------|
| Represents 24.1 per cent of the total carbon.  |  | Contains 75.9 per cent of the total carbon. |
| Identity of components unknown.                |  |                                             |
| The alkaline solution, acidified and filtered. |  |                                             |
| Precipitate.                                   |  | Acid filtrate.                              |
| Represents 36.9 per cent of the total carbon.  |  | Contains 39.0 per cent of the total carbon. |
| Extracted with boiling alcohol.                |  | Would contain if present:—                  |
| Insoluble.                                     |  | Dihydroxystearic acid.                      |
| Represents 15.7 per cent of the total carbon.  |  | Xanthine.                                   |
| Identity of components unknown.                |  | Hypoxanthine.                               |
| Alcohol solution.                              |  | Cytosine.                                   |
| Contains 21.2 per cent of total carbon.        |  | Histidine.                                  |
| Extracted with petroleum ether.                |  | Arginine.                                   |
| Insoluble.                                     |  | Pentosan.                                   |
| Represents 19.1 per cent of the total carbon.  |  |                                             |
| Would contain, if present:—                    |  |                                             |
| Resin acids.                                   |  |                                             |
| Resin esters.                                  |  |                                             |
| Petroleum ether solution.                      |  |                                             |
| Contains 2.1 per cent of the total carbon.     |  |                                             |
| Would contain, if present:—                    |  |                                             |
| Hydroxystearic acid.                           |  |                                             |
| Paraffinic acid.                               |  |                                             |
| Lignoceric acid.                               |  |                                             |
| Glycerides.                                    |  |                                             |
| Agrosterol.                                    |  |                                             |
| Phytosterol.                                   |  |                                             |

In actual practice it has been found that treatments that will promote oxidation either in the soil itself, as by aeration, cultivation, or drainage, or the application of lime or nitrates which stimulate biological oxidation, whether by roots or otherwise, tend to the destruction of this compound.

Finally, the work reported here shows that while the chemistry of the soil organic matter is complex it is not hopelessly so. As was stated in the introduction, no systematic attempt has as yet been made to account by isolated compounds for all of the organic matter in the soils studied. However, in one soil this is so nearly approached that it is offered as an illustration of what has been accomplished in this direction. This is represented in Chart C. A soil containing 0.955 per cent organic carbon was extracted in quantities of 10 grms. with 2 per cent sodium hydroxide solution until no more organic matter was extracted, the soil washed free of alkali, and the carbon determined in the residue. The solution was treated as indicated. Some of the figures

were, of course, obtained by difference, and all of the compounds mentioned did not occur in this soil, but are named in the place where they would be found if present.

The two fractions with unknown components making 39.8 per cent of the total carbon have been but slightly investigated. It has been found, however, that the portion insoluble in alcohol, on again dissolving in alkali and repeating the separation with alcohol, is much reduced in quantity, a portion being rendered soluble in alcohol and transferred to the portion insoluble in petroleum ether. In the soil examined, the portion soluble in petroleum ether, 2.1 per cent of the total carbon, was wholly accounted for in isolated compounds, as was the portion insoluble in petroleum ether and representing 19.1 per cent of the total carbon. The portion in the acid filtrate in the case of most soils represents 40 to 50 per cent of the total carbon, and contains a considerable quantity of unidentified material, in addition to the large number already isolated and identified.



SUMMARY.

In this Bulletin is given some definite knowledge of the nature of the organic compounds in the soil, and methods are described by which a number of organic compounds have been isolated from soils.

The compounds obtained have been described and the manner in which they have been identified pointed out, the possible sources of the compounds suggested, and their relation to other compounds stated.

In a previous Bulletin the isolation of four organic compounds from soils was described: Dihydroxystearic acid,  $C_{18}H_{36}O_4$ ; picolinic carboxylic acid,  $C_7H_7O_2N$ ; agroceric acid,  $C_{21}H_{42}O_3$ ; and agosterol,  $C_{26}H_{44}O \cdot H_2O$ . The compounds in this Bulletin, sixteen in number, are shown to belong to eight different classes of chemical compounds, some containing carbon and hydrogen only, some containing carbon, hydrogen, and oxygen, and some containing carbon, hydrogen, oxygen, and nitrogen. Paraffin hydrocarbons, acids, alcohols, esters, carbohydrates, hexone bases, pyrimidine derivatives, and purine bases are represented. The list of isolated and identified compounds comprises: Hentriacontane,  $C_{31}H_{64}$ ; monohydroxystearic acid,  $C_{18}H_{36}O_3$ ; paraffinic acid,  $C_{24}H_{48}O_2$ ; lignoceric acid,  $C_{24}H_{48}O_2$ ; phytosterol,  $C_{26}H_{44}O \cdot H_2O$ ; pentosan,  $C_5H_{10}O_4$ ; histidine,  $C_6H_9O_2N_3$ ; arginine,  $C_6H_{14}O_2N_4$ ; cytosine,  $C_4H_5ON_3 \cdot H_2O$ ; xanthine,  $C_5H_4O_2N_4$ ; hypoxanthine,  $C_5H_4ON_4$ ; fatty glycerides, and several resin acids and esters.

The conclusion is reached that while the work here reported shows the complex character of the organic matter of soils, this complexity is not so great that the chemical nature of all of the organic matter of soils can not be determined by modern methods of research.

THE AFTER-GLOW IN VACUUM TUBES.

THE HON. R. J. STRUTT lectured before the Röntgen Society on February 6th on the subject of the after-glow or perceptible luminosity seen in vacuum tubes after the electrical discharge has been shut off. This phenomenon, he said, was not a mere luminosity of the walls of the tube, and it only became conspicuous when the pressure was very high, as in the case of vacuum tubes designed to bring out the spectra of different gases. He carried out a number of experiments at the meeting, using a vacuum tube with electrodes, an air-pump, and a stop-cock for admitting the gas which rushed through the tube at high speed. He employed, in the first place, ordinary atmospheric air, and showed that the vessel remained luminous after the discharge had passed through. By substituting pure oxygen for air, however, this phenomenon of luminous after-glow on the cessation of the discharge appeared no longer. In the case of air enriched with oxygen the glow at first was more brilliant than with normal air, and afterwards less brilliant. Thus while oxygen was unable by itself to produce the glow, nitrogen, when mixed with oxygen, could produce it. Prof. Strutt's explanation was that when an electric discharge passed through a mixture of oxygen and nitrogen it produced ozone from the oxygen, and also produced nitric oxide, and that these two substances combined in the vessel to form a kind of flame. He passed oxygen through the vessel, and instead of relying on the discharge itself to produce nitric oxide, he admitted ready-made nitric oxide by a side-tube, whereupon the yellow flame due to the chemical combination of the nitric oxide with the ozone was found to be produced much more brilliantly. When the purest nitrogen was allowed to go through the vessel the flame produced had a characteristic brownish yellow colour, being quite different in tint from the yellow glow produced by ozone and nitric oxide. The result of admitting the ready-made nitric oxide into the nitrogen was to produce a yellowish-green glow of exactly the same kind as that obtained by allowing the nitric acid to come into

contact with the ozone. The lecturer regarded the glow produced by nitrogen alone as being a kind of unstable flame, due to a new modification of nitrogen produced by the discharge. A great many chemical substances could be stimulated to luminosity by contact with the active nitrogen. Acetylene, for example, combined with the active nitrogen and produced the cyanogen flame. The vapour of chloride of tin was equally stimulated, and a brilliant blue flame was the result. His own impression was that in some cases, with iodine for example, there was no chemical combination, although there was a remarkable spectrum, while in other cases, as with acetylene, the chemical combination was beyond all doubt. A curious phenomenon was noted in connection with the nitrogen spectra. In the ordinary vacuum spectrum of nitrogen there appeared a perfectly definite series of bands in the yellow region, which most people would think were inseparably connected together. But in the spectrum of the glow caused by the active nitrogen re-combining, some of the bands exactly corresponded with those in the ordinary nitrogen spectrum, while others were altogether absent. The spectrum of the active nitrogen in the process of combination was the ordinary nitrogen spectrum with great pieces of it left out, like "a mouth with some of the teeth missing." Prof. Strutt stated that in all cases in which the nitrogen acted on metals and gave metallic spectra chemical combination was produced.

BORON IN THE PREPARATION OF CARBORUNDUM.

DR. E. G. ACHESON, whose work upon Graphite and Carborundum is well known, has recently been granted the following patent for the manufacture of a refractory body with novel properties. (Application filed May 27, 1909, Serial No. 498,643, Patented Jan. 9, 1912).

To all whom it may concern:

Be it known that I, Edward Goodrich Acheson, a citizen of the United States, residing in Stamford township, Welland county, Province of Ontario, Canada, have invented certain new and useful improvements in Refractory Bodies and Processes of Making Same, of which the following is a specification.

This invention relates to a novel electric furnace product or series of products of refractory character and extreme hardness, such products containing silicon and carbon as essential constituents, but differing in certain highly important respects from the crystallised silicid of carbon known as carborundum.

As is well known, the crystallised silicid of carbon known as carborundum is an extremely hard and rather brittle body consisting essentially of silicon and carbon in proportions corresponding to the formula  $SiC$ . This body is produced commercially by heating a mixture of sand and coke, or other form of carbon, by means of an embedded resistor, usually consisting of granular coke. To increase the porosity of the charge sawdust is commonly added, and it is also customary to add sodium chloride, whereby the elimination of iron is facilitated.

I have now discovered that under certain conditions it is possible to obtain a product which contains silicon and carbon, and may perhaps consist essentially of these elements in substantially or even precisely the proportions in which they exist in carborundum, this new product differing however in essential respects, and particularly in certain physical characteristics, from carborundum. The distinction which I regard as most important and most characteristic of the novel product is in respect to its greater toughness or lesser degree of brittleness, in which respect it far excels carborundum. This novel product is formed by a reaction occurring in the electric furnace between sand or equivalent silicious material and carbon, in presence of

an element or compound capable of modifying the reaction to such degree or in such manner that the product acquires the essential physical characteristic of increased toughness as compared with carborundum. As an example of its production I will describe the following:—A mixture was prepared consisting essentially of pure silica sand and carbon commingled in the proportions theoretically required for the production of silicide of carbon, that is to say in the proportion of 62·7 parts of sand to 37·3 parts of carbon. To this mixture was added a second mixture consisting essentially of boric acid from which most of the water of crystallisation had been expelled, and carbon, the boric acid and carbon being in the approximate proportions of 210 parts of  $B_2O_3$  to 120 parts of carbon. These two mixtures were thoroughly commingled in various proportions, the proportions in one specific instance being 92 parts of the silica mixture to 8 parts of the boric acid mixture. The resulting mass was heated in an electric furnace of the resistance type, being disposed in proximity to the resistor and carefully shielded from the action of the air. The temperature was approximately that required for the production of carborundum, and was maintained for several hours. At the close of the operation the product was found to consist in part of a crystalline material, much of which presented the appearance of plates of considerable size with very thin and sharp edges, clearly distinguishable from the comparatively blunt edges of typical carborundum crystals. The material was black in colour or nearly so, and did not in this instance exhibit the iridescent colouring which is often characteristic of carborundum. The hardness of the new product is at least equal to and perhaps greater than that of carborundum. The specific gravity of one specimen of the product in the form of highly developed crystals was 3·246, closely approximating that of carborundum. The temperatures of formation and decomposition of the product appear to be similar to those for carborundum. Upon decomposition at high temperatures a residue of graphite remained. The product was also observed in the form of masses wherein no crystalline structure was apparent, these masses being very dense in character and presenting the appearance of having undergone at least partial fusion.

The most striking and salient characteristic of the product, both in the crystalline and massive forms, is, as above stated, its toughness as compared with carborundum. This characteristic toughness of the material, in conjunction with its extreme hardness, indicates abrasive qualities of exceptional value.

Boron may enter into the product of the furnace operation, but whether in case it so enters it exists in chemical combination with the silicon and carbon, or as a carbide of boron in admixture with silicide of carbon, or in admixture therewith in other form or combination, is not at present known. It appears probable however from the results obtained that the product may be entirely or substantially free from boron either in combination or admixture, and may yet exhibit in a high degree those valuable properties above noted and those characteristics which distinguish it from carborundum, such properties and characteristics being presumably in this case due to the modifying influence, during the reaction, either of the boric anhydride or of the products of reduction thereof. In such case it is reasonable to suppose that other bodies may prove capable of exerting a like favourable effect upon the toughness of the product.

I claim:

1. The herein described novel product, containing as essential constituents silicon and carbon, and characterised by a degree of toughness exceeding that of carborundum.

2. The process which consists in disposing in proximity to a resistor a charge containing a silicious material, carbon and a compound of boron, the compound of boron in less proportion than the silicious material, and effecting reduction of the same by heat developed in said resistor by the passage therethrough of an electric current, thereby

producing a material containing as essential constituents silicon and carbon, and characterised by a degree of toughness exceeding that of carborundum.

In testimony whereof, I affix my signature in presence of two witnesses.

EDWARD GOODRICH ACHESON.

Witnesses:

W. H. ARISON,  
EBEN C. SPEIDEN.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

Ordinary Meeting, February 1st, 1912.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"Bacterial Production of Acetylmethylcarbinol and 2,3-Butylene Glycol from Various Substances." By ARTHUR HARDEN, F.R.S., and DOROTHY NORRIS.

*B. lactis aerogenes* and *B. cloacæ*, when grown in a peptone solution containing either glucose, lævulose, mannose, galactose, arabinose, isodulcitol, or adonitol, produce both acetylmethylcarbinol and 2,3-butylene glycol.

Glycerol, ethylene glycol, and acetaldehyde under similar conditions also give rise to butylene glycol in presence of *B. lactis aerogenes*, but no acetylmethylcarbinol is produced.

In these three cases a carbon synthesis is involved analogous to that which occurs in the butyric fermentation of glycerol and lactic acid.

The fermentation of citric and malic acids, of dihydroxyacetone, and of peptone water give rise to neither carbinol nor glycol.

"Chemical Action of *Bacillus cloacæ* (Jordan) on Glucose and Mannitol." By JAMES THOMPSON.

The *B. cloacæ*, like *B. lactis aerogenes*, produces a considerable proportion of 2,3-butylene glycol from glucose and mannitol, as well as a small amount of acetylmethylcarbinol. The other products are alcohol, acetic, lactic, formic, and succinic acids, carbon dioxide, and hydrogen. As in the cases of *B. lactis aerogenes* and *B. coli communis*, the percentage of alcohol produced from mannitol is about double that formed from glucose.

"Distribution of the Nerves of the Dental Pulp." By J. H. MUMMERY.

"Method for Isolating and Cultivating the Mycobacterium Enteritidis Chronica Pseudo-tuberculosis Bovis (Föhne), and some Experiments on the Preparation of a Diagnostic Vaccine for Pseudo-tuberculosis of Bovines." By F. W. TWORT, M.R.C.S. (Eng.), L.R.C.P. (Lond.), and G. L. Y. INGRAM, M.R.C.V.S.

"Fossil Flora of the Forest of Dean Coalfield (Gloucestershire) and the Relationship of the Coalfields of the West of England and South Wales." By E. A. N. ARBER.

"Simultaneous Colour Contrast." By F. W. EDRIDGE-GREEN, M.D., F.R.C.S., Beit Memorial Research Fellow.

1. The colours and changes of colour which are seen on simultaneous contrast appear to be due to the exaggerated perception of objective relative differences of the contrasted lights. Whilst all the known contrast phenomena are easily explicable on this view, there are many facts which are opposed to the older theories. For instance, spectral yellow or pigment yellow contrasted with green do not appear red when seen through a blue-green glass which is impervious to the red rays.

2. A certain difference of wave-length is necessary before simultaneous contrast produces any effect. This varies with different colours.



3. A change of intensity of one colour may make evident a difference which is not perceptible when both colours are of the same luminosity.

4. Simultaneous contrast may cause the appearance of a colour which is not perceptible without comparison.

5. Both colours may be affected by simultaneous contrast, each colour appearing as if moved further from the other in the spectral range.

6. Only one colour may be effected by simultaneous contrast, as when a colour of low saturation is compared with white.

7. When a false estimation of the saturation or hue of a colour has been made, the contrast colour is considered in relation to this false estimation. That is to say, the missing (or added) colour is deducted from (or added to) both.

8. A complementary contrast colour sensation does not appear in the absence of objective light of that colour.

"*Studies on Enzyme Action. XIV.—Urease, a Selective Enzyme.*" By Prof. H. E. ARMSTRONG, F.R.S., and E. HORTON.

SOCIETY OF CHEMICAL INDUSTRY.  
(LONDON SECTION).

Ordinary Meeting, February 5th, 1912.

Mr. E. GRANT HOOPER in the Chair.

THE following papers were read and discussed:—

(I.) "*Constant Temperature Heating Apparatus for Explosives*," and (II.) "*Experiments on the Decomposition of Nitro-cellulose in Vacuo*." By J. S. S. BRAME.

The apparatus is designed to obviate the use of liquid baths with their accessories, heating by the vapour of a liquid of constant boiling-point being employed. By the condensation and return of the liquid to the boiler, the apparatus is automatic and capable of application wherever constant heating of small quantities of a substance is required. From the boiler the vapour may be short-circuited through a ball valve, then the condenser and back to the boiler, and when the liquid is boiling freely the vapour may be sent through one or both of the double-walled copper heaters in which the decomposition tubes are placed, the ball valve cutting off the short circuit.

For application in the case of the decomposition of nitro-cellulose, 2 grms. of the sample are heated in each tube after exhaustion for six hours, the evolved gases remaining in the tube; the pressure is then read off on a manometer, and, finally, the gases pumped out and measured.

Experiments conducted at 110°, 115°, and 130° C. on samples of gun-cotton, soluble and highly soluble cottons, showed that the gas evolution at 110° was very small and the results erratic. At 115° there is a very large gas evolution from poor samples of trinitro-cellulose, but this temperature is not sufficiently high to differentiate between a fairly good and high class product.

The best of the gun-cottons and all the soluble and highly soluble samples were treated at 130°, and the gas evolution with the best samples was from four to five times as great as at 115°, with poorer samples as much as ten times.

Comparison with the Will test with selected pairs in each series show that the smaller differences between the samples, known to exist from the amount of purification undergone, is more clearly shown than with the Will test, doubtless due to the accelerating action of the products of decomposition.

"*Some Physical Properties of Structureless Cellulose Filaments (Artificial Silk)*." By W. P. DREAPER and J. G. DAVIS.

It is an accepted fact that the knowledge gained from the study of the physical properties of structureless filaments, notably of cellulose in the form of artificial silk,

has proved of great industrial value. The increase of the tenacity and the decrease of the ultimate percentage elongation occurring with decreasing size (denier) of filament has been demonstrated by numerous tests.

A comparison of the test-data of representative specimens, obtained under similar conditions, has led to the conclusion that this is due to the surface condition of the material, namely, to the presence of a "skin" which is relatively harder and more tenacious than the core, and which bears a larger proportion to the total cross section of small filaments than of large ones.

The conclusions arrived at from the experimental curves are identical with those which would arise from the assumption of constancy of skin thickness for all sizes of filaments manufactured under like conditions.

Empirical formulæ obtained from tests on composite threads (19—160 denier), all of forty-five filaments, give a mean value for the tenacity or ultimate strength ( $f$  max) in grammes per denier (see Note) of the composite thread of—

$$f \text{ max} = 6.70 \text{ (deniers)} - 0.38 \quad \dots (1),$$

and for the final percentage elongation ( $E$  max) a mean value of—

$$E \text{ max} = 2.77 \text{ (deniers)} 0.41 - 6 \quad \dots (2),$$

comparing with tests on monofilaments or single filaments up to 300 deniers each.

Conditions of manufacture modify the above constants, and the laws can only be taken as applying within the experimental range mentioned, both probably changing in nature on attainment of a condition equivalent to that of "solid skin."

Numerous tests on monofilaments of squirted cellulose have indicated the similarity existing between the stress-strain relations of these and of drawn metallic filaments, such as copper, the elastic and plastic stages being strongly marked, as also the local contraction at fracture; thus similar results are obtained with presumably simple and complex molecules. The value of  $E$  increases considerably in finer filaments, but a mean value roughly  $1/40$  that for mild steel is found to hold.

Sufficient tests have also been made under conditions of periodic loading to illustrate the analogy between the behaviour of single filaments of cellulose and of ductile metals in such circumstances.

(NOTE.—A 10,000 metre length of 1 denier filament weighs, by definition, 1 gram. Thus the experiments cover a range of variation in the individual filaments of the composite threads of 0.422—3.56 grms. per 10,000 metres).

## NOTICES OF BOOKS.

*A Text-book of Physiological Chemistry.* By OLOF HAMMARSTEN. Authorised translation from the Seventh German Edition by JOHN A. MANDEL, Sc.D. Sixth Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1911. (17s. net).

THE translation of Hammarsten's "*Text-book of Physiological Chemistry*" has been widely used in England and America, and the many biochemists who have been in the habit of constantly using it as a book of reference will be glad to have a new edition, in which all the latest data and the most recent results are included. A new chapter on physical chemistry in biology, by Prof. S. G. Hedin, of Upsala, has been added. In it osmotic pressure, colloids, catalysis, enzymes, ions, and salt action are fully discussed, with special reference to biochemistry. Some other alterations have been made, including the incorporation of the chapter on the Animal Cell in other chapters. The book has unavoidably considerably increased in size, and all the text has undergone a thorough revision.

*The Chemical World: a Monthly Journal of Chemistry and Chemical Engineering.* Vol. I., No. 1. London: Messrs. J. and A. Churchill. (6d. net).

THE aim of the new monthly journal, *The Chemical World*, is to provide an account of the progress of all branches of chemistry, both as regards theory and practice, and to follow the development of research in the pure and applied science. The first number augurs well for the future, and the journal will receive a hearty welcome from its scientific contemporaries. The list of contributors is a strong one, and their articles cover a wide range of subjects. The illustrations are an attractive feature, those in the first number including several reproductions of photographs of the laboratories of the Royal College of Science, the work and equipment of which is discussed in the first of a series of articles on the Chemical Departments of modern Universities and Technical Colleges.

*A Text-book of Practical Chemistry for Technical Institutions.* By A. E. DUNSTAN, D.Sc. (Lond.), and F. B. THOLE, B.Sc. (Lond.), F.C.S. London: Methuen and Co., Ltd. 1911. (3s. 6d.).

THIS is a remarkably cheap book, and many lecturers and demonstrators will be glad to recommend it to their students. It contains the complete five-year course of practical chemistry, which is worked through by the science students of the East Ham Technical College, and covers the syllabuses of the Intermediate and Final University Examinations and the examinations of the Institute of Chemistry. Qualitative analysis is first treated in great detail; formulæ and equations are given in abundance, and the theory of analytical work is briefly discussed; the rarer elements which are of technical importance are included. In the chapters on quantitative work, volumetric and gravimetric analysis are fully treated, and a few typical technical analyses are also described, while a short course of organic analysis and of the preparation of common organic substances finds a place towards the end of the book. In addition, directions are given for a few of the important operations of physical chemistry, such as the determination of molecular weights, and conductivity, and work with the polariscope. The authors have made good use of the standard works on the various branches of their subject, and have compiled an indisputably valuable book.

*Boiler Draught.* By H. KEAY PRATT, M.I.Mech.E. London: Constable and Co., Ltd. 1911. (4s. net).

IN this little book special attention is paid to the mathematical work which has to be done in order to determine whether a given arrangement for producing a boiler draught is the most economical and satisfactory that can be devised. Many numerical examples are worked out in full to explain the formulæ given, and nothing beyond a working knowledge of very elementary mathematics is necessary to follow the calculations. The treatment of the subject is thoroughly practical, and the author does not hesitate to give his views concerning cases in which he believes that discrepancies exist between the results of theory and practice. In a chapter on the chemistry of combustion, methods of analysing furnace gases are briefly discussed, and again the working out of results is fully explained. The book gives a useful survey of the most efficient working of steam plants, both from the point of view of altering existing arrangements to make them more satisfactory, and of planning new plant.

**Royal Institution.**—On Saturday, February 24th, at 3 o'clock, Prof. Sir J. J. Thomson will begin a course of six lectures at the Royal Institution on "Molecular Physics." The Friday Evening Discourse, on February 23rd, will be delivered by Mr. G. K. B. Elphinstone, on "The Gyrostatic Compass and Practical Applications of Gyrostats"; on March 1st, by Dr. W. J. S. Lockyer, on "The Total Solar Eclipse in the South Pacific, April, 1911"; and on March 8th, by Dr. A. W. Ward, on "The Effects of the Thirty Years' War."

## CORRESPONDENCE.

### CANADIUM.

*To the Editor of the Chemical News.*

SIR,—Your issue of December 15th, 1911, was most interesting, containing, as it did, an account from Mr. French of the possible discovery of a new element to which he gave the name "Canadium." This supposed element he found associated with platinum, iridium, rhodium, and osmium in the Nelson district of British Columbia.

A subsequent letter from Mr. Eastick, in the *CHEMICAL NEWS* of January 19th, 1912, refers to a notice by Courtis, which appeared in the *Transactions* of the American Institute of Mining Engineers in 1903, concerning a new element, "amarillium," which he said occurred in a copper carbonate ore from Similakameen, British Columbia, and which Courtis considered a link between the platinum-palladium, and nickel-cobalt groups.

Working some years ago on concentrates which contained the elements above-named, *i.e.*, practically all the metals known in Group VIII., which had their origin in Canada, although not in the district of British Columbia, the writer was much struck by various anomalies.

These were mostly apparent in separating palladium by the usually employed analytical methods. The idea was recorded as to the possibility of an unknown element or elements being present, and notes were made of various reactions and properties, *e.g.*, formation of highly coloured salts and easy fusibility. The idea was approached, however, with much caution, since palladium forms very stable alloys with various metals, notably with copper, platinum, iridium, rhodium, and gold, which alloys behave almost as a single metal, although alone palladium acts very differently to these separate metals or its alloys with them.

The notice regarding the discovery of canadium will act as a stimulus in proceeding further with this work.—I am, &c.,

WM. HAMILTON PATTERSON.

Monksferry Laboratory,  
Birkenhead.

## MEETINGS FOR THE WEEK.

MONDAY, 19th.—Royal Society of Arts, 8. (Cantor Lecture). "The Meat Industry," by Loudon M. Douglas, F.R.S.E.

TUESDAY, 20th.—Royal Institution, 3. "The Study of Genetics," by Prof. W. Bateson, F.R.S.

WEDNESDAY, 21st.—Royal Society of Arts, 8. "The British Silk Industry and its Development since 1903," by Frank Warner.

Microscopical, 8. "Fourth List of New Species of Rotifera since 1889," by C. F. Rousselet. "Colouring of Lantern Slides," by E. J. Spitta.

THURSDAY, 22nd.—Royal Institution, 3. "The Portraiture of Shakespeare," by M. H. Spielmann, F.S.A.

Royal Society, 4.30. "Variation of the Specific Heat of Water Investigated by the Continuous Mixture Method" (the Bakerian Lecture), by H. L. Callendar. "Index to Reports of Physical Observations—Electric, Magnetic, Meteorological, Seismological—made at Kew Observatory," by C. Chree. "Velocities of Ions in Dried Gases," by R. T. Lattey and H. T. Tizard. "Observation by means of a String Electrometer of Fluctuations in the Ionisation produced by  $\gamma$ -Rays," by T. H. Laby and P. W. Burdige. "The Wave Problem of Cauchy and Poisson for Liquid of Finite Depth and for Slightly Compressible Liquid," by F. B. Pidduck.

FRIDAY, 23rd.—Royal Institution, 9. "The Gyrostatic Compass and Practical Applications of Gyrostats," by G. K. B. Elphinstone, M.Inst.E.E.

Physical, 5. "Method of Accurate Comparison of Quantities of Radium," by Prof. E. Rutherford and Mr. Chadwick. "Absorption of the  $\gamma$ -Rays by Gases," by Mr. Chadwick. "On Wave-form Sifters for Alternating Currents," by A. Campbell.

SATURDAY, 24th.—Royal Institution, 3. "Molecular Physics," by Sir J. J. Thomson, F.R.S., &c.



# THE CHEMICAL NEWS.

VOL. CV., No. 2726.

## BICENTENARY ANNIVERSARY OF M. V. LOMONOSOFF'S BIRTHDAY.

By B. N. MENSCHUTKIN

(Concluded from p. 75).

### II.

I WILL give now a very succinct account of Lomonosoff's work on physics and chemistry as the more important. A prominent place in it is taken by physical and chemical theoretical conceptions; developed by means of the mathematical philosophy and based on the mechanical laws they closely resemble modern theories, and form important landmarks in the history of science. Almost all these theories are deductions made from the fundamental atomic theory, which, strange to say, was never published by Lomonosoff, but several accounts of which, belonging to the years 1742-1744, have been preserved among his manuscripts. In substance it is as follows:—

All material bodies consist of minute particles imperceptible to the senses resulting from physical division. Each particle (*particula physica insensibilis*) has exceedingly small but finite dimensions, possesses all the properties of a solid body, and is subject to mechanical laws. In these particles lies the cause of all bodily properties—elasticity, density, &c., and such phenomena as heat and cold. All these phenomena can be explained by mechanical laws applied to the motions of the particles. The particles themselves are round, very hard, elastic, and have on their surface infinitely small asperities.

This theory was applied by Lomonosoff first of all to the phenomena of heat, and the results given in his paper, "*Meditationes de Caloris et Frigoris Causa*" (written in 1744-1745, published in 1750). He begins by giving some experiments tending to show that a sufficient cause of heat lies in movement. As no motion of the whole body is observed when it is heated the motion must be invisible, *i.e.*, must belong to the physical particles. Of the three possible motions—progressive, oscillatory, and gyratory—only the last can be assumed to be the cause of heat, for the two first are incompatible with the nature of a solid body. All the phenomena of heat can be accounted for by that assumption. When, for instance, a warm body is brought into contact with a cold one, the first communicates a part of the motion of its particles to those of the second. In accordance with mechanical laws the motions of the particles of the warm body become slower, those of the particles of the cold one quicker, and the warm body begins to cool, the cold one to get warmer. As the rotary motion of the particles becomes more violent, centrifugal forces are developed which tend to drive the particles asunder; that is the reason why a body melts if sufficiently heated. Therefore liquid bodies, still more gaseous ones, have always a heat motion, even if they seem to be very cold.

Such are Lomonosoff's views about heat; they are very remarkable for his time, when the substance of heat (caloric) was assumed by everybody to be the cause of heat. The notion of caloric was held, as is known, till the second half of the Nineteenth Century, and was given up only after the mechanical nature of heat was demonstrated by Rob. Mayer and others.

Even more interesting is Lomonosoff's theory of the gaseous state, given in the paper, "*Tentamen Theoriæ de vi Aeris Elasticæ*" (1748). Its fundamental idea is taken from D. Bernoulli's "*Hydrodynamica*" (1738), where the author, in order to deduce the laws of the flow of elastic

liquids, assumes that the air consists of little corpuscles, moving about with great rapidity. Lomonosoff's theory is as follows:—

All the properties of air make it certain that it is composed of minute particles, which may be called atoms. Air can be compressed to one-thirtieth part of its original volume; therefore the atoms cannot be in touch with each other; on the other hand, they cannot act on each other without coming in contact. These two necessarily true but contradictory consequences can be reconciled only by the assumption, that at a given moment of time not all the atoms are in the same state, and each state continues only during an infinitesimal fraction of time; the atoms collide with each other and rebound in all directions after collisions. As all the atoms have rotary heat motion, at collision their minute asperities make them rebound one from the other, and that is the mechanical cause of their mutual resilience. The atoms have a very small but finite mass and weight; consequently they fall towards the centre of the earth; existing in countless numbers it is impossible that each should fall just on the top of the other, therefore they fly back in all directions, and the elasticity of air shows itself everywhere. Thus the atmosphere consists of an infinitely great number of atoms flying in all directions, continually colliding with each other and rebounding, again colliding and rebounding, and so on. This constitution of the atmosphere is also demonstrated by the propagation of sound, which is nothing but the wavelike movement of the atoms of air.

This theory is, as we see, nothing else but the modern kinetic theory of gases. A hundred years after Lomonosoff, in 1845, the same views were brought forward by Waterstone, but only after the work of Clausius and Krönig (1856-1857) this theory began to gain favour in the scientific world. Needless to say that Lomonosoff's theory was completely forgotten, and was brought to light only some years ago.

The investigations of Lomonosoff did not end here; in a supplement to his theory (1750) he went a step further. He shows that when air is subjected to pressure the atoms are brought nearer together, collide more frequently, the number of collisions and the elastic force of air augmenting with the pressure and rising proportionately with the diminution of volume. But the atoms themselves have a certain volume; therefore under great pressures the collisions will be proportionately more numerous and the resistance of the air greater, so that the greater the pressure the larger the difference between the actual volume of air and that computed by assuming a simple proportionality between pressure and volume.

As is well known, it was only more than one hundred later that A. Dupré (1864) and then Van der Waals (1873) thought it necessary to take into consideration the finite dimensions of the atoms and molecules.

I will now briefly mention other physical work of Lomonosoff. During the great frosts of December, 1759, when the temperature descended at St. Petersburg to  $-41^{\circ}$  C., his friend, the academician, J. Braun, made on Christmas Day the discovery that quicksilver could freeze; together with Lomonosoff they investigated the properties of frozen mercury, and the latter left us a description of all these experiments in his allocution on the fluidity and solidity of bodies (1760).

Electricity was an object of many of his researches; I will mention only Lomonosoff's theory of formation of atmospheric electricity. The first notes relating to it we find in May, 1751, and the theory itself was published in 1753. He attributes the formation of electricity to the friction of atoms of the air and the water-vapour, occurring during the vertical movements of air in the atmosphere. These vertical movements Lomonosoff attributed to the rise of warm air and to the fall of cold air of the upper atmosphere; the first is generally the cause of formation of thunderclouds, the second of such electric displays as aurora borealis. These theories were confirmed by experimental determinations of the expansion of air, with rise

and fall of temperature and observations of thunderstorms, during one of which the academician, Richmann, while repeating the experiments of Franklin, was killed by the lightning (July, 1753), and Lomonosoff himself narrowly escaped a like fate.

Before I come to speak of the chemical work of Lomonosoff, I must remind the reader that the years 1748-1756, which witnessed most of his chemical investigations, belong to that period in the history of chemistry, which is characterised by the implicit belief in the theory of phlogiston, when such phenomena as burning, oxidation, &c., were all explained by means of that fanciful element. Another characteristic of this time is the absence of quantitative chemical experiments. The views of Lomonosoff on chemistry as a whole are very broad and surprisingly modern.

His first contribution to chemistry dates from 1741, and is the beginning of a treatise, which was never finished, "*Elementa Chymiae Mathematicae*." Chemistry is defined here as a science of the changes occurring in the composed bodies; the chemist must possess historical as well as philosophical knowledge of these changes; all that he asserts he must prove by means of experiments; a chemist must ever be a philosopher. As all the changes are produced by the motions of particles, he must also be conversant with the laws of mathematics and mechanics to be able to deduce chemical laws from those of the motions of particles. It is very interesting to note that Lomonosoff draws in his "*Elementa*" a severe distinction between the atoms, which he names "primary corpuscles," and molecules, "derivative corpuscles, consisting of several primary ones," and says that the quantitative relations of the chemical elements (he calls an element "*principium*") in a composed body is just the same as in its derivative corpuscule. He states further that one of the causes of the diversity of chemical bodies lies in the different arrangement of primary corpuscles constituting a derivative corpuscule. It was only in 1829 that Berzelius came to this conclusion and founded the conception of isomerism; and only the second half of the Nineteenth Century saw the chemists beginning to distinguish atoms from molecules.

Lomonosoff's chemical conceptions changed somewhat in the course of time. In 1749, in his "*Dissertatio de Nitro*," occurs the following passage:—"We think it possible to expound scientifically chemistry . . . and have no doubt that by considering together all chemical and physical truths we can gain more knowledge of the hidden nature of chemical bodies. If we state the chemical truths so that one may see at a glance how one truth is evolved from another, or explained by it, we will be able to judge what other natural sciences have given to chemistry . . . after that this sublime science will surely occupy a fitting place among other physical sciences." The same idea of the close relationship between chemistry, physics, and mathematics is expressed in a popular form in his allocution "On the Usefulness of Chemistry," thus, "Chemistry must be called the right hand of physics, mathematics—its eyes."

This conception of chemistry he upheld to the end of his life, and contributed himself as much as he could to the development of "physical chemistry," as he called it. In 1751-1753 Lomonosoff held in the University lectures on this subject, part of which is contained in his MSS., "*Tentamen Chymiae Physicae in Usum Studiosae Juventutis Adornatum*, 1752." Physical chemistry is defined in Sect. 1 of this Tentamen as follows:—"Physical chemistry is a science, explaining by means of laws and experiments of physics the changes produced by chemical operations in compound bodies. It may be called chemical philosophy, but is quite different from the mystic philosophy, where not only no explanations are given, but the operations themselves are conducted in secret."

These views of a chemist of the middle of the Eighteenth Century are most remarkable. Physical chemistry, as a separate science, has developed itself only during the last

decades, and it is only a few years ago that the courses of physical chemistry were being held in the Universities, and higher mathematics began to form a necessary subject in the education of a chemist. The enormous progress of physical chemistry shows how well Lomonosoff understood, 150 years ago, the conditions necessary for the development of chemistry as an exact science.

The experimental work of Lomonosoff is also full of interest. The important feature of it is that all his chemical work is strictly quantitative, and in his lectures he always enforced the necessity of using everywhere measure and weight. The physico-chemical experiments—the first ever performed with the intention of using them for the development of physical chemistry—were proposed on a very large scale; no less than four different programmes of them have come down to us. To show their comprehensive nature I will give here Lomonosoff's programme for the investigation of the solutions: (1) How much of different salts water dissolves at different temperature; (2) the densities of these solutions; (3) changes in volume during dissolution; (4) the lowering of temperature produced by the dissolution; (5) expansion of solutions from  $0^{\circ}$  to  $150^{\circ}$ ; (6) boiling-points of solutions; (7) heat capacity of solutions; (8) dissolution of salts in saturated solutions of other salts; (9) freezing points of solutions; (10) refractive index of solutions compared with that of water; (11) the rise of solutions in capillary tubes; (12) microscopical investigations of solutions; (13) the changes brought about in solutions by electrical force. Many workers of to-day investigate the questions enumerated in this vast programme, of course without knowing that they are executing the programme drawn up 150 years ago by Lomonosoff! The temperatures in it are given in degrees of Lomonosoff's thermometer. This thermometer had  $0^{\circ}=0^{\circ}$  Celsius and  $150^{\circ}=100^{\circ}$  Celsius, so that each degree of Lomonosoff is equal to two-thirds of the degree of Celsius.

It is evident that an investigation of all the points proposed, even only for solutions, would take many years to accomplish; that is one of the causes why Lomonosoff himself, with his pupils, could not do it. Another cause lies in the complete absence of quantitative methods in experimental chemical work of these days—for instance, the analytical methods which we now use almost exclusively in physico-chemical work were then unknown. Still many quantitative investigations, dealing chiefly with sections 1, 4, and 6 of the programme given above, were made, as is known from the yearly reports presented by Lomonosoff to the Academy. Unfortunately the original laboratory journals could not be found, so that it is now impossible, from the few numerical values which have reached us, to form an exact notion of the work done. The solubilities of salts in water were determined, on the whole, approximately correctly for the lower temperatures, but are much too small for higher temperatures—doubtless a result of increasing experimental difficulties. As Lomonosoff expressly states, all the salts for these investigations were carefully purified and crystallised several times. He was aware of the fact that the pure compounds have fixed properties, not depending on the method of their preparation.

We will now turn our attention to another series of Lomonosoff's experiments—to those relating to the phenomena of burning and calcination. They occupied him from the year 1742 onwards; but it is only in 1745 that we find in the "*Meditationes de Caloris et Frigoris Causa*" his views. After mentioning the experiments of R. Boyle, who observed the increase of weight of calcinated bodies and explained it by the combination of them with the ponderous substance of flame, Lomonosoff comes to the conclusion, as a result of experiments, that *this increase is due to the air*, which always flows round a body when it is subjected to calcination and combines with it.

But this conclusion seemed incompatible with other experiments of R. Boyle (1673), where calcination of lead was carried out in hermetically sealed glass retorts. After these retorts had cooled down Boyle opened them—to see if they were hermetically closed—and on weighing them invariably



found an increase of weight. Lomonosoff therefore repeated these experiments in 1756 with the following results: "I made experiments in hermetically sealed glass vessels in order to investigate if the weight of metals is augmented by heat alone. These experiments showed that the opinion of the famous Robert Boyle is false, because without letting in the outward air the weight of the burnt metal and of the vessel remains the same." These experiments showed that his views on calcination as a combination of metal with air were correct. He intended to publish all these experiments in the paper, "De Incremento Ponderis per Calcinationem," but it could not be found among his MSS., so that it is uncertain if he ever wrote it. The same experiments of R. Boyle were repeated seventeen years after Lomonosoff by Lavoisier (1773) with identical results.

I have no doubt that the quantitative methods employed by Lomonosoff enabled him to verify a very important law, the law of conservation of matter, which he exposed for the first time in a letter, dated July 5th, 1748, to his friend, the celebrated mathematician, Leonhard Euler, who was also a member of the Russian Academy of Sciences, in the following manner: "All changes taking place in Nature proceed thus: if anywhere something is added the same amount is taken away in another place. Thus, if one body receives an increase of matter another body loses just as much. This law of Nature is universal and applicable also to the laws of motion."

This universal law of conservation of matter and energy, the foundation of the modern physics and chemistry, was probably taken by Lomonosoff from philosophical treatises, and was applied by him everywhere; here is an instance of it. In his paper, "Dissertatio de Actione Menstruorum Chymicorum in Genere" (1745), he describes the mechanism of dissolution in Sect. 44 and 45 thus:—In the process of a solid passing into a liquid the particles of the solid accelerate their motion. When a salt deliquesces in water, the movements of the salt particles are accelerated by the faster motions of the water particles; but one body can accelerate the motion of another body, and communicate to it a part of its own motion only if it itself loses the same amount of motion. Therefore the water particles, having given part of their motion to the salt particles, move now more slowly; but as motion is the cause of heat water must get colder, and we actually observe this during the dissolution of a salt.

During the twelve years since Lomonosoff communicated this law to Euler, he found it confirmed in the part relating to the conservation of matter in all his chemical experiments, and therefore published it in 1760, in the same words that he employed in his letter to Euler, in the paper on the fluidity and solidity of bodies. Needless to say that it was absolutely unnoticed, and the first enunciation of the principle of conservation of matter is usually ascribed to Lavoisier (1789).

In conclusion, I may state that Lomonosoff did not believe in phlogiston, the properties of which defied quantitative determinations; he used it in some of his allocutions to make himself better understood by his hearers, familiar with the fundamental chemical theory of the day—and in some dissertations presented to the Academies of Petersburg and Berlin, where at that time many chemists were personal friends of Stahl, the founder of the phlogistic theory.

Lomonosoff's ideas on chemistry were more than a century ahead of his time, and we cannot but call him in all justice the first physico-chemist.\*

Gosnowka Polytechnical Institute,  
St. Petersburg, October 1st, 1911.

\* His works on physics and chemistry are printed in volume VI. of his collected works, edited by the Russian Academy of Sciences. This volume contains his printed dissertations and all MSS. notes, and will appear at the end of this year. I have also translated into German Lomonosoff's important physical and chemical papers, and supplied them with notes; they appeared as No. 178 of Ostwald's "Klassiker" in 1910 (Leipzig, Engelmann).

# ON THE BECKMANN REARRANGEMENT.\*

## II.

By MITSURU KUHARA and YOSHINORI TODO.

For the explanation of the Beckmann rearrangement, several theories have been proposed up to this time by different chemists, but none of them is likely to lead to a satisfactory generalisation owing to the present incomplete state of investigation:—

|                           |                                                 |
|---------------------------|-------------------------------------------------|
| Beckmann .. .. .          | Ber., xxvii., 300.                              |
| Stieglitz .. .. .         | Am. Chem. Journ., xviii., 751; xxix., 49.       |
| Nef .. .. .               | Ann. der Chem., cccxviii., 227.                 |
| Slosson .. .. .           | Am. Chem. Journ., xxix., 289.                   |
| Werner and Piquet ..      | Ber., xxxvii., 4295.                            |
| Sluiter .. .. .           | Rec. Trav. Chim., xxiv., 372.                   |
| Wallach .. .. .           | Ann. der Chem., cccxvi., 272.                   |
| Diels and Stern .. .      | Ber., xl., 1631.                                |
| Schröter .. .. .          | Ber., xlii., 2236.                              |
| Stieglitz and Peterson .. | Ber., xliii., 782.                              |
| Montagne .. .. .          | Rec. Trav. Chim., xxv., 376; Ber., xliii., 204. |

By the measurement of the velocity in the rearrangement of methylphenylketoxime through the action of sulphuric acid, which was performed by Sluiter (*Rec. Trav. Chem.*, xxiv., 372) by determining the amount of acetic acid, liberated from acetanilide formed in the reaction, by its saponification, there was obtained a constant which shows the reaction to be monomolecular. The author's attention was directed to the same line of investigation in a somewhat different way, by ascertaining the influence of different acid chlorides upon the rate of rearrangement of diphenylketoxime, and the velocity of its rearrangement by acetyl chloride as well as that of acetyldiphenylketoxime by hydrochloric acid.

For the study of the influence of different acid chlorides, acetyl, monochloroacetyl, and benzenesulphonyl chlorides were taken. In each experiment acid chloride and diphenylketoxime were allowed to react on each other in molecular proportions at 60°, each substance having been dissolved in chloroform so as to make half molar solution. After a definite interval of time the benzanilide produced was carefully isolated and its quantity determined. The following table shows the comparative amounts of benzanilide formed from diphenylketoxime by different acid chlorides:—

| Time (minutes). | Per cent benzanilide formed by— |                            |                           |
|-----------------|---------------------------------|----------------------------|---------------------------|
|                 | Acetyl chloride.                | Monochloroacetyl chloride. | Benzenesulphonyl chloride |
| 10              | 0                               | 61.0                       | 93.2                      |
| 15              | 2.4                             | —                          | —                         |
| 30              | 9.4                             | 66.1                       | —                         |
| 60              | 26.9                            | 70.7                       | —                         |
| 90              | 37.2                            | 74.9                       | —                         |
| 120             | 43.9                            | 76.9                       | —                         |

As seen from the table, diphenylketoxime did not change at all into benzanilide by acetyl chloride in ten minutes, but in fifteen minutes only 2.4 per cent, while by monochloroacetyl chloride more than half, and by benzenesulphonyl chloride nearly all of its quantity suffered rearrangement in ten minutes. Hence the rate of rearrangement must be dependent upon the degree of acidity of the acid from which a chloride is derived; in other words, upon the nature of the negative character of the acid residue, R'COO—, coupled in oxime ester that may be formed by acid chloride. Thus, the relative strengths of acetic, monochloroacetic, and benzenesulphonic acids from which three respective chlorides are derived, as arranged in the

\* *Memoirs of the College of Science and Engineering, Kyoto Imperial University*, ii., No. 12.

order of their dissociation constants, are found to be concordant with the rate of rearrangement:—

| Acids.                 | K.                  |
|------------------------|---------------------|
| Acetic acid            | 0.000018            |
| Monochloroacetic acid  | 0.001550            |
| Benzenesulphonic acid. | Immeasurably great. |

For the measurement of the velocity of rearrangement of diphenylketoxime which would be effected by acid chloride the authors took acetyl chloride and diphenylketoxime in molecular proportions and dissolved each in dry chloroform so as to make half molar solution at 60°. Both solutions, taken in 5 cc. each and mixed in a sealed tube at 0°, were allowed to remain in a thermostat at the temperature of 60°. After a certain interval of time the sealed tube was taken out from the thermostat, and its contents transferred into a beaker, and the chloroform removed by blowing dry air through the solution. Before setting the sealed tube in a thermostat, and after removing it from the same, it was kept in ice-cold water in order to arrest the progress of reaction. The residue obtained by the evaporation of chloroform was treated with 20 per cent solution of sodium hydroxide, filtered, and washed well with water. The benzanilide left as a residue by such a treatment was dissolved in alcohol, and the solution then filtered was allowed to evaporate. The residue, consisting of benzanilide was dried at 110° and its weight ascertained. By such a process of treatment we were able to isolate from the products all of benzanilide in a pure state, which was judged from its right melting-point of 158–159°.

Inferring the nature of reaction from the results of experiment the change would actually belong to the type of monomolecular reaction, as a velocity constant has been obtained by the calculation with the well-known equation for that of the first order—

$$0.4343 k = \frac{1}{t} \log \frac{a}{a-x}$$

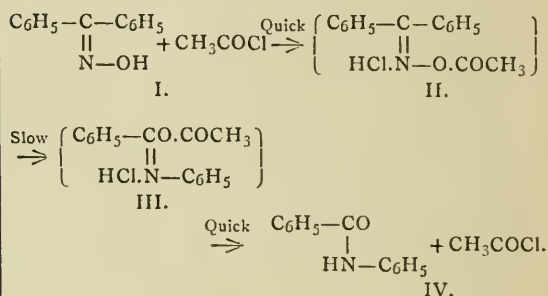
as will be shown in the following table, the initial disturbance being possibly due chiefly to the influence of the temperature of the contents in the sealed tube which must take a certain interval of time to be equalised with that of the thermostat.

| t (min.) | x    | $\frac{1}{t} \log \frac{a}{a-x}$ | $\frac{1}{t-15} \log \frac{a-x_{15}}{a-x}$ |
|----------|------|----------------------------------|--------------------------------------------|
| 15       | 2.4  | 0.00070                          |                                            |
| 30       | 9.4  | 0.00143                          | 0.00215                                    |
| 40       | 14.9 | 0.00175                          | 0.00238                                    |
| 50       | 20.6 | 0.00200                          | 0.00256                                    |
| 60       | 26.9 | 0.00227                          | 0.00228                                    |
| 90       | 37.2 | 0.00224                          | 0.00229                                    |
| 120      | 43.9 | 0.00209                          | 0.00213                                    |
| 180      | 61.0 | 0.00227                          | 0.00241                                    |
| 240      | 69.0 | 0.00212                          | 0.00221                                    |
| 360      | 78.2 | 0.00184                          | 0.00188                                    |
| 480      | 88.9 | 0.00198                          | 0.00203                                    |
|          |      | 0.00210                          | 0.00223                                    |

Moreover, the rearrangement of acetyldiphenylketoxime by hydrochloric acid has been studied. For this purpose acetyldiphenylketoxime was dissolved in a saturated solution of hydrochloric acid in chloroform at 0°, whose strength had previously been ascertained by titration in such a way as to correspond to each other in molecular proportions. 10 cc. of the solution were taken, and heated in a sealed tube by immersing into a bath of boiling water. After a certain interval of time the content of the tube was treated in the same way as in the previous experiments, and the quantity of benzanilide produced was determined. As will be seen in the results here stated in the following table, the reaction is also of monomolecular type.

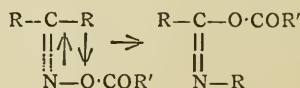
| t (min.) | x    | $\frac{1}{t} \log \frac{a}{a-x}$ |
|----------|------|----------------------------------|
| 20       | 27.4 | 0.00695                          |
| 30       | 37.5 | 0.00680                          |
| 40       | 44.3 | 0.00635                          |
| 60       | 56.1 | 0.00596                          |
| 90       | 76.4 | 0.00697                          |
| 120      | 80.0 | 0.00583                          |
|          |      | 0.00648                          |

Interpreting the mechanism of rearrangement from the statements so far recorded, the authors propose for its explanation to represent the change by the following scheme with a slight modification to the previous one (*Memoirs*, vol. i., 255).

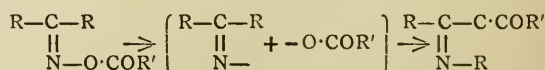


As the authors have to regard the scheme by Sluiter (*loc. cit.*) with respect to the progress of rearrangement as correct, in the present case by analogy the change of the system I. to II. is regarded as quick, II. to III. as slow, and III. to IV. as quick, and as a consequence only the velocity in the second phase of reaction (II. to III.) should be measurable; therefore the nature of reaction in the rearrangement must be observed to be monomolecular as a matter of course. The view on the mechanism of rearrangement proposed as above may further be explained, based upon the assumptions which will be described hereinafter.

I. Rearrangement of ketoxime may be due to an interchange of positions between a hydrocarbon radical linked to carbon and an acid residue attached to nitrogen in an oxime ester formed in reaction—

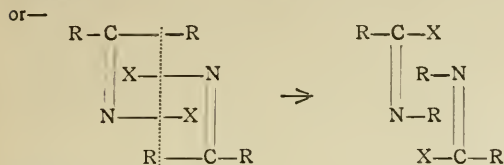


As the primary cause of such an interchange, the authors take account of the tendency of an acid residue to separate from nitrogen which, when it has been strengthened under the influence of temperature, but in some cases by a joint action with acid, may cause its dissociation,\* by which the shifting of a hydrocarbon radical to nitrogen by its effort to occupy a more favoured position, and as a consequence the transposition of the acid residue to carbon are possible to be brought about; therefore the change may be looked upon as the effect of a process like double decomposition, which takes place within a molecule or between two molecules—



\* Nef has applied his theory of dissociation to the explanation of the Beckmann rearrangement, but its scheme is different from that proposed by the authors.—*Ann. der Chem.*, cccxviii., 227. According to Beckmann's view the process consists in the transposition of electrically charged radicals or ions, but the reagent merely acts as a catalyser by increasing the velocity of interchange (*Ber.*, xxvii., 300).

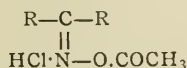




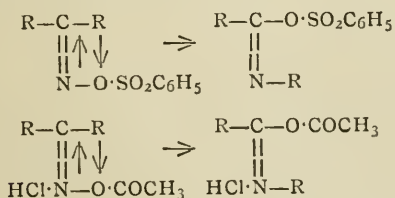
in which  $\text{X} = \text{R}'\text{CO}\cdot\text{O}-$ .

Such a mobility of acid residue is considered to stand in a close connection with the strength of its negative character; that is, the more negative the acid residue the looser may be its linking to nitrogen, rendering the system more liable and more prone to rearrangement; hence it is regarded that in the rearrangement of diphenylketoxime by acetyl, monochloroacetyl, and benzenesulphonyl chlorides, the acid residues,  $\text{CH}_3\cdot\text{CO}\cdot\text{O}'$ ,  $\text{CH}_2\text{ClCO}\cdot\text{O}'$ , and  $\text{C}_6\text{H}_5\text{SO}_2\cdot\text{O}'$ , in their respective ethers may change their positions more or less readily, in proportion to the strength of their negative character, namely, in the order of benzenesulphonyl, monochloroacetyl, and acetyl oximes, as the experiments on the rate of rearrangement show.

Beckmann (*Ber.*, xxvii., 2583) states that diphenylketoxime and methylphenylketoxime yield, by the action of acetyl chloride, their acetyl ethers, which at all events undergo rearrangement, when hydrochloric acid, liberated in the reaction, is allowed to come completely to action; and also it has been shown by one of us and Kainosho (*Memoirs*, &c., vol. i., 254), as well as by the authors, that pure acetyldiphenylketoxime actually needs the presence of hydrochloric acid for its rearrangement, while several oximes (*Ber.*, xxiv., 3539, 4162, 4167; xxxvii., 4295), such as diphenylketoxime, benzamidoxime, benziloximes, &c., readily undergo rearrangement in presence of alkali or pyridine by the action of benzenesulphonyl chloride, although hydrochloric acid liberated in the reaction is immediately removed by alkali or pyridine. Hence, in the case of acetyl oximes, hydrochloric acid must be a necessary reagent for rearrangement, but in the case of benzenesulphonyl oximes, the transposition of the benzenesulphonic acid residue may simply be effected without the aid of hydrochloric acid. For such a difference of the behaviours of acetyl and benzenesulphonyl oximes the authors put forward an explanation based upon the assumption that in benzenesulphonyl oxime the benzenesulphonic acid residue,  $\text{C}_6\text{H}_5\text{SO}_2\cdot\text{O}'$ , may readily separate from nitrogen on account of its strong negative character, while in the case of acetyl oximes, their hydrochlorides,—



may be formed on account of the relatively weak negative character of the acetic acid residue,  $\text{CH}_3\text{CO}\cdot\text{O}'$ , but the latter group getting more negative under the influence of hydrochloric acid added to nitrogen may increase its tendency to separate from the latter, and eventually its migration may be effected—

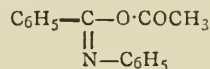


It has been noticed by the authors, as already stated, that at the temperature of  $60^\circ$ , the rearrangement of diphenylketoxime by the action of acetyl chloride progresses moderately, while that of pure acetyldiphenylketoxime by hydrochloric acid is exceedingly slow, but very rapid at the temperature of boiling water, although in both cases the

hydrochloride of acetyldiphenylketoxime ought to suffer the change equally under the same condition. The authors have now to explain such a phenomena by assuming that in the former case the elements of hydrochloric acid may act in a nascent state upon acetyldiphenylketoxime formed in the reaction, yielding its hydrochloride, but in the latter the hydrochloric acid present in a free state may need high temperature for the formation of the salt.

2. It is evident, from the experiments by one of us and Kainosho (*Memoirs*, &c., vol. i., 254), that hydrochloric acid may actually take part of reaction in the change of acetyldiphenylketoxime formed as an intermediate product in the rearrangement of diphenylketoxime, because, as a matter of fact, hydrochloric acid and acetyldiphenylketoxime have to react on each other always in equivalent proportions. Thus their experiments show that when the different quantities of hydrochloric acid are allowed to act upon the same definite quantity of pure acetyldiphenylketoxime, the quantity of the resulting benzanilide is equivalent to that of hydrochloric acid taken, if its quantity is smaller than enough to be equivalent to that of the oxime ester used, as the formation of new hydrochloric acid is not effected in the case of the ester, the acetyl chloride produced remaining unchanged, but to the quantity of oxime ester, if hydrochloric acid is present, more than enough to be equivalent to that of the oxime ester. Such a relation of the interacting substances, therefore, stands in harmony with the assumption in respect to the second and third phases of the reaction in rearrangement, as is seen from the scheme of mechanism already represented.

3. In this laboratory S. Kodama has lately succeeded in isolating a compound which must possess a constitution corresponding to the formula,—



by treating benzimidochloride,  $\text{C}_6\text{H}_5-\text{CCl}=\text{N}-\text{C}_6\text{H}_5$ , with silver acetate. It is a thick yellow oily substance of unstable nature. By passing dry hydrochloric acid through its ethereal solution cooled with a freezing mixture, its hydrochloride separates out as a canary-yellow precipitate, but by the excess of the acid changes to acetylbenzanilide\* and other compounds by molecular rearrangement. The hydrochloride dissolved in chloroform and heated in a sealed tube above  $60^\circ$  yields benzanilide at once; hence its decomposition is assumed to correspond to the last phase of the process of rearrangement. Matter about that compound has not been published yet, as its investigation is now going on.

## QUICK COMBINATION METHODS IN SMELTER ASSAYS.†

By A. T. FRENCH.

THE smelter chemist is usually called upon to do daily analyses of one or more ores or products which form the furnace charge, and also of the slag. The chief constituents to be determined are, for the furnace charge:—

Insoluble ( $\text{SiO}_2$ ), Fe,  $\text{Al}_2\text{O}_3$ , CaO, Zn, Pb, S, and Cu;

for slags:—

Insoluble: Fe,  $\text{Al}_2\text{O}_3$ , CaO, Zn, and Cu.

Many methods of determining the separate elements are given in text-books and in technical literature. It is the

\* O. Mumm states that he has obtained acetylbenzanilide by treating benzimidochloride with sodium acetate, but nothing is said about such a compound as Kodama has prepared (*Ber.*, xliii., 886).

† A Paper discussed at a Meeting of the Institution of Mining and Metallurgy, held at the Rooms of the Geological Society, Burlington House, Piccadilly, W., on Thursday, February 15th, 1912.

object of this paper to present a scheme for the combination of these methods, which has been worked out by the author with considerable trial and experiment, and which seems of sufficiently general application to merit the attention of those members of the Institution who are interested in similar work.

The problem, then, is the separation of the above elements and oxides from each other, and their estimation in the presence of such usual constituents of ore as As, Sb, Mn, MgO, &c.

A standard of accuracy of 0.5 per cent is required (*i.e.*, iron, if reported 20 per cent must be within 19.75 to 20.25), except in the case of copper, which should be within 0.1 or 0.2 on ores and 0.025 on slags.

#### Method "A" for Ores.

Weigh out two  $\frac{1}{2}$  gram. for the analysis and  $\frac{1}{2}$  or 1 gram. for sulphur.

The two  $\frac{1}{2}$  gram. for analysis are moistened with water, 5 to 10 cc. of strong  $\text{HNO}_3$  are added, and taken to dryness on the hot plate; 5 cc. of  $\text{HCl}$  are added to each, and after a few minutes' digestion at a moderate temperature 20 cc. of dilute  $\text{H}_2\text{SO}_4$  (1:3), and the assays are rapidly boiled down to white fumes. After cooling and dilution with water to about 100 cc., to (1) 5 cc. of  $\text{HCl}$  are added, and to (2) 10 cc. of dilute  $\text{H}_2\text{SO}_4$ , and both are boiled a few minutes.

In (1) Insoluble,  $\text{SiO}_2$ , Fe, CaO, and Zn are to be estimated.

In (2) Pb, Cu, and  $\text{Al}_2\text{O}_3$ .

(1) *Insoluble*.—The hot solution is filtered through an ashless paper and washed thoroughly with hot water, the filtrate is removed and the residue washed with a hot solution of ammonium acetate (if much lead is present it is better to wash back into the beaker, add ammonium acetate, and digest for a few minutes on the hot plate, finally throwing back on to the same filter); the washings are thrown away, and the filter with contents is placed on a roasting dish, dried, ignited in the muffle, and, after cooling, weighed as "insoluble."

The filtrate in a 600 cc. beaker is diluted with hot water to 300 to 400 cc., about 10 grms. of pure ammonium chloride added, and, if manganese is present, 10 to 20 cc. of strong bromine water, then an excess of  $\text{NH}_4\text{HO}$ . The solution is brought to a boil, the precipitate allowed to settle and then filtered, washing with hot water, or, better, if much zinc is present, with a hot dilute ammoniacal solution of ammonium chloride. The filtrate and washings are received in a litre beaker, and the hydrate precipitate is re-dissolved in  $\text{HCl}$  and re-precipitated as before (not forgetting the bromine water, if necessary) in a rather smaller bulk, combining the two filtrates.

*Iron*.—The hydrate precipitate is either re-dissolved in dilute  $\text{H}_2\text{SO}_4$ , the iron reduced and titrated cold with standard potassium permanganate, or the precipitate is dissolved in  $\text{HCl}$ , reduced, and titrated with standard potassium bichromate.

*Lime*.—To the combined filtrates 20 to 30 cc. of a 2 per cent solution of ammonium oxalate are added, the solution is brought to a boil and allowed to stand in a warm place for half-an-hour, by which time the calcium oxalate should be settled out and the solution clear. The calcium oxalate is filtered off, washed thoroughly, dissolved in warm dilute sulphuric acid, diluted with hot water, and titrated hot with standard potassium permanganate.

*Zinc*.—The filtrate from the calcium oxalate is acidified with  $\text{HCl}$ , adding 5 cc. in excess. A current of  $\text{H}_2\text{S}$  is passed through it for five to ten minutes, the solution is then boiled for five minutes, filtered, if necessary (usually this is not the case), cooled to about  $30^\circ\text{C}$ ., and titrated with standard potassium ferrocyanide.

(2) This portion is allowed to stand until quite cold in order that the lead sulphate may separate out and settle. It is then filtered, washing by decantation with cold water, and adding a little dilute  $\text{H}_2\text{SO}_4$  to the wash-water from time to time,

*Lead*.—To the residue in the beaker are added 5 to 10 grms. of ammonium acetate, a little acetic acid, and 100 cc. of hot water. The filter paper is dropped into it and the beaker placed on the hot plate, brought to a boil, and, when all the lead sulphate is dissolved, about another 100 cc. of hot water is added, and the solution is titrated hot with standard ammonium molybdate.

The filtrate, to which a little strong  $\text{HCl}$  may be added, is heated to near boiling, and a current of  $\text{H}_2\text{S}$  is passed for ten minutes. The sulphides are filtered off, using a rapid filter, and washed with hot water ( $\text{H}_2\text{S}$  water should be used if the filtrate comes through at all cloudy, but this is rarely the case).

*Copper*.—The sulphides are washed back into the beaker, opening out the filter paper and placing it on the side of the beaker; a few drops of bromine water are poured over it to oxidise the traces of sulphides retained in the pores of the paper; then 5 cc. of  $\text{HNO}_3$  and a little hot water, and the paper is removed. A small quantity of iron is added, about 0.05 gram., the beaker is placed on the hot plate and boiled down to dryness. After cooling, 2 or 3 cc. of  $\text{HCl}$  are added, and the copper estimated by the permanganate method.

*Alumina*.—A filtrate from the sulphides is boiled to expel  $\text{H}_2\text{S}$ , oxidised with 2 or 3 cc. of  $\text{HNO}_3$ , a slight excess of  $\text{NH}_4\text{HO}$  is added, and the solution boiled until it no longer smells of  $\text{NH}_4\text{HO}$ . After standing a minute or two to settle the hydrates are filtered off, washed slightly, washed back into the beaker, and re-dissolved in a little  $\text{HCl}$ , pouring the acid first over the filter paper. The solution is just neutralised with  $\text{NH}_4\text{HO}$ , 2  $\frac{1}{2}$  to 2 cc. of  $\text{HCl}$  are added, and the alumina is estimated by the phosphate method.

*Sulphur*.—On silicious and burnt ores 1 gram. is taken, on pyritic ores  $\frac{1}{2}$  gram., moistened with water, and about 5 grms.  $\text{KClO}_3$  and 10 cc.  $\text{HNO}_3$  added. The assay is taken to near dryness on the hot plate, avoiding baking, taken up with 5 to 10 cc. acetic acid (1:1) and 150 to 200 cc. of hot water; about 10 grms. of ammonium acetate are added, the solution is brought to a boil and titrated, boiling, with standard barium chloride.

*Examination of "Insoluble" Silica*.—(1) When the "insoluble" is white, as in treating most raw ores and others easily attacked by acids, the residue obtained in the first part of the analysis is fused in a platinum dish or crucible with ten times its weight of fusion mixture ( $\text{K}_2\text{CO}_3$  and  $\text{Na}_2\text{CO}_3$ ). The melt is dissolved in  $\text{HCl}$ , transferred to a porcelain capsule or casserole, taken to dryness on the hot plate, taken up with 5 to 10 cc.  $\text{HCl}$ , diluted, and the silica filtered off, dried and ignited. After cooling in a desiccator the  $\text{SiO}_2$  is weighed, and an addition made for the  $\text{SiO}_2$  still left in solution (see Expt. 12). The filtrate from the  $\text{SiO}_2$  is rendered slightly ammoniacal, the solution boiled until it no more smells of  $\text{NH}_4\text{HO}$ , and, after standing a few minutes, the hydrates are filtered off, washing thoroughly with hot water. The filter and contents are dried, ignited, and weighed, reporting as  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$ .

(2) When the insoluble is black or red, as in treating burnt ores and substances not easily attacked by acids, the residue is fused as in (1) and the  $\text{SiO}_2$  filtered off, ignited, and weighed.

The filtrate is tested for Cu and Pb by passing  $\text{H}_2\text{S}$ . If any is found the sulphides should be filtered off, dissolved in  $\text{HNO}_3$ , taken to fumes with  $\text{H}_2\text{SO}_4$ , diluted and cooled; the  $\text{PbSO}_4$  is filtered off and added to the main portion, and the copper in solution also added to the main portion obtained in the first part of the analysis before precipitation with ammonium sulphocyanide. (The free sulphuric acid should be just neutralised with  $\text{NH}_4\text{HO}$ ).

The filtrate from the sulphides, or from the silica in absence of Cu and Pb, is boiled to expel  $\text{H}_2\text{S}$ , oxidised with  $\text{HNO}_3$  or  $\text{KClO}_3$ ,  $\text{NH}_4\text{HO}$  is added until the solution darkens, or, in absence of much iron, until the solution is only very faintly acid, and 5 to 10 grms. of sodium acetate are added. The solution is brought to a boil,



allowed to stand, and the precipitated basic acetates of iron and alumina are filtered off.

After washing with hot water the acetates are washed into a porcelain dish, about 1 inch of caustic soda or potash added, and digested at a gentle heat for a quarter of an hour. The  $\text{Al}_2\text{O}_3$  goes into solution, the iron precipitate is filtered off, re-dissolved, reduced and titrated as in the first part of the analysis.

The filtrate is acidified with HCl, and the  $\text{Al}_2\text{O}_3$  either estimated by the phosphate method or a slight excess of  $\text{NH}_4\text{HO}$  is added, boiled off, the precipitate filtered off, dried, ignited, and weighed as  $\text{Al}_2\text{O}_3$ .

(If the quantity of iron and alumina is large, the acetates should be dissolved in HCl and re-precipitated with  $\text{NH}_4\text{HO}$ , boiling off excess before extracting with caustic, but usually this can be omitted.)

**Lime.**—To the filtrate from the acetates about 10 cc. of  $\text{NH}_4\text{HO}$  and 20 cc. of a 2 per cent solution of ammonium oxalate are added, and the calcium oxalate precipitated and filtered off. This precipitate is dried and ignited, weighing as  $\text{CaO}$ ; it should be tested for iron, and, if any is found, the weight of  $\text{Fe}_2\text{O}_3$  is subtracted from the  $\text{CaO}$ , and the calculated amount of Fe added to that previously found.

**Zinc.**—The filtrate from the lime is acidified, gassed, boiled, cooled, and titrated with standard potassium ferrocyanide.

#### Method "B" for Slags.

The sample should be chilled—this is usually done at the furnace, the molten sample of slag being poured into a bucket of water. Otherwise the slag in lump form may be heated to redness in the muffle and thrown into water before grinding, the effect being to make the slag easily attacked by acids, anything up to 50 per cent  $\text{SiO}_2$  giving a white insoluble containing not more than 1 to 2 per cent of substances other than silica.

For the analysis two  $\frac{1}{2}$  grm. are weighed into 300 cc. beakers or casserroles. The slag is moistened with 2 to 3 cc. of water, the beaker is held over a spirit lamp, keeping the contents in motion, and when near boiling 3 cc. of strong HCl are added and a few drops of  $\text{HNO}_3$ . The heating is continued for two to three minutes, when gelatinous silica separates out, and the beaker may be placed on the hot plate and taken to complete dryness.

**Insoluble.**—The two portions are taken up with 5 cc. HCl, diluted to about 100 cc. with hot water, and the insoluble filtered off (use of the filter-pump is unnecessary if the  $\text{SiO}_2$  has been properly dehydrated), dried, ignited in the muffle, and weighed.

Filtrate (1) is diluted to about 300 cc. with hot water, about 10 grms. of  $\text{NH}_4\text{Cl}$  are added, and bromine water of manganese is present, and then  $\text{NH}_4\text{HO}$  in excess. The solution is boiled, the precipitate allowed to settle, then filtered into a litre beaker, washing with hot water; the hydrates are re-dissolved in HCl,  $\text{NH}_4\text{Cl}$  and bromine water (if necessary) added, re-precipitated with  $\text{NH}_4\text{HO}$  and filtered off, combining the two filtrates.

**Iron.**—The hydrate precipitate is re-dissolved in dilute  $\text{H}_2\text{SO}_4$ , reduced and titrated with standard permanganate, or HCl may be used, and the solution, after reduction, titrated with bichromate.

**Lime.**—To the combined filtrates, which should be strongly ammoniacal, 20 cc. of a 2 per cent solution of ammonium oxalate are added, the solution brought to a boil, and allowed to stand in a warm place until the calcium oxalate settles. This is then filtered off, washed, dissolved in dilute  $\text{H}_2\text{SO}_4$ , and titrated hot with standard permanganate.

**Zinc.**—The filtrate from the lime is acidified with HCl, adding 5 cc. in excess, a current of  $\text{H}_2\text{S}$  is passed for five to ten minutes, and the solution is boiled, cooled to about  $30^\circ\text{C}$ ., and titrated with standard potassium ferrocyanide.

**Alumina.**—Filtrate (2) is just neutralised with  $\text{NH}_4\text{HO}$ , 2 to 3 cc. of HCl are added, and the alumina estimated by the phosphate method. If much Cu and Pb, &c., are present the filtrate should be gassed, filtered,  $\text{H}_2\text{S}$  boiled off,

and the solution oxidised before proceeding as above; but the author has not found this to be necessary in dealing with ordinary slags.

**Copper.**—For copper 5 grms. are weighed into a 600 cc. beaker, about 250 cc. of hot water added, and the beaker placed on the hot plate. When boiling 30 cc. of strong HCl are carefully added, and the solution stirred until decomposition is complete. If pure acid has been used the sulphides of Cu, &c., which are not attacked can be filtered off, but it is safer to pass  $\text{H}_2\text{S}$  for a few minutes before filtering. The sulphides are washed back into the same beaker, cleaning the paper with bromine water, and dissolved in  $\text{HNO}_3$ . The copper is then usually estimated by titration with cyanide or colorimetrically. A more accurate, though rather longer, method is to take to complete dryness, take up with HCl, and estimate the copper by the permanganate method.

(To be continued)

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

Ordinary Meeting, February 8th, 1912.

Sir ARCHIBALD GEIKIE, K.C.B., President, followed by Sir ALFRED KEMPE, Vice-President and Treasurer, in the Chair.

PAPERS were read as follows:—

"*Spectrum of Comet Brooks (1911 c).*" By Sir NORMAN LOCKYER, K.C.B., F.R.S.

In this paper an account is given of the lines shown in a series of ten photographs of the spectrum of Comet Brooks, taken between September 6th and October 31st. Seven of the photographs were taken while the comet was an evening object, and three when it was a morning object. The instrument used was a two-inch quartz-calcite prismatic camera.

In the best spectrum (September 30th), in addition to the well-established carbon or carbon-compound bands at  $\lambda\lambda$  3883, 4737, 5165, 5635, other radiations were seen at  $\lambda\lambda$  310, 316, 337, 405, 421, and 436. Line  $\lambda$  421 is probably the cyanogen band, the head of which is  $\lambda$  4216.

So far as is known, the ultra-violet bands  $\lambda\lambda$  310, 316, 337 have not been recorded in the spectrum of any previous comet. Attempts have been made to ascertain the chemical origin of these lines by reference to published records of laboratory spectra, and to recent photographs of the spectrum of CO taken with the quartz-calcite prism, but with no success.

Although no definite changes in the relative intensity of the cometary lines were noted amongst the earlier photographs, a comparison of the best of these (September 30th) with that of October 31, when the comet was a morning object, showed the following changes:—

1. On September 30th line  $\lambda$  4216 was weakest of the three subsidiary lines  $\lambda\lambda$  405, 4216, 436. On October 31st it was strongest.

2. Lines  $\lambda\lambda$  3883, 4737 were of about equal intensity on September 30th. On October 31st  $\lambda$  3883 was distinctly the stronger.

3. The ultra-violet lines  $\lambda\lambda$  310, 316, 337 shown in the spectrum of September 30th, were not seen on October 31st.

A photographic comparison is given of the Kensington spectrum of Comet Brooks (September 30th) with that of Comet Daniel (1911 d), reproduced by Campbell in *Lick Bulletin* No. 135. Although the latter showed far more detail, being photographed with a slit spectrograph, it is fairly evident that the spectra of the two comets are very similar.

"A Chemically Active Modification of Nitrogen, produced by the Electric Discharge. (III.)" By Hon. R. J. STRUTT, F.R.S.

1. Active nitrogen emits its energy more quickly, and reverts sooner to ordinary nitrogen, if it is cooled. This is apparently a unique instance of a chemical change accelerated by cooling.

2. If the glowing gas is compressed to small volume, it flashes out with great brilliance, and exhausts itself in so doing. This proves that the glow-transformation is poly-molecular, *i.e.*, that more than one molecule must take part in it.

3. Active nitrogen may revert to ordinary nitrogen in two distinct ways. One of those is a volume change, accompanied by glow; the other a surface action of the walls of the vessel, without glow. This is analogous to the behaviour of oxy-hydrogen gas in its transformation to water, which may be a surface or volume effect, according to circumstances.

"Atomic Weight of Radium." By R. WHITLAW-GRAY and Sir W. RAMSAY, K.C.B., F.R.S.

The material for this research consisted of 330 mgrms. of a mixture of radium and barium bromides, containing 206 mgrms. of radium bromide, supplied by the courtesy of the British Radium Corporation. The bromides were submitted to methodical fractional crystallisation, and yielded specimens of which the change in weight on conversion from bromide to chloride with gaseous hydrogen chloride, and from chloride to bromide with gaseous hydrogen bromide, was determined with the micro-balance. The atomic weight increased progressively from 220.7, through a series of approximations, to the final atomic weight 226.36, the last five determinations giving the figures 226.40, 226.25, 226.35, 226.35, and 226.45.

The paper contains remarks on the differences in terms of multiples of the atomic weight of helium between the recorded determinations of the atomic weight of uranium and radium on the one hand, and of radium and lead on the other; and it is pointed out that a careful revision of the atomic weights of lead and of uranium, especially of the latter, is much to be desired.

"Emission of Electricity from Carbon at High Temperatures." By Dr. J. A. HARKER, F.R.S., and Dr. G. W. C. KAYE.

This paper discusses several new phenomena, among which are the generation of electric currents of considerable magnitude by what appears to be a new method. Two insulated carbon electrodes are inserted into a carbon tube resistance furnace at high temperatures, and are connected externally through a suitable current-measurer. If one of the electrodes is suddenly displaced to a colder or hotter part of the furnace, a reversible transient current is produced in the circuit without the application of any external potential. By such means currents up to 2 amperes have been obtained. The production of an alternating current is thus rendered possible by the use of a suitable periodic device.

A continuous current can be generated by suitably modifying the apparatus so as to maintain a large permanent temperature-difference between the electrodes. A steady current of 0.8 ampere has been thus obtained for a few minutes, and 0.1 ampere for over an hour by water-cooling one electrode.

These currents are such as would be produced by a discharge of negative particles from the hot electrode. At the lower temperatures positive currents have also been detected, but of much smaller magnitude. All the observations were made at atmospheric pressure.

The extent of the ionisation of the furnace atmosphere at high temperatures was such that quite small E.M.F.'s, applied to two exploring electrodes, gave rise to steady currents of relatively enormous magnitude. For example, with 8 volts, currents up to 10 amperes have been obtained at a temperature of about 2500° C.

Some of these observations have been repeated with furnaces of a non-electric character.

"The so-called Thermoid Effect and the Question of Superheating of a Platinum-silver Resistance used in Continuous-flow Calorimetry." By Prof. H. T. BARNES, F.R.S.

"Optical Determination of the Variation of Stress in a Thin Rectangular Plate subjected to Shear." By E. G. COKER, M.A., D.Sc.

The distribution of stress in a rectangular plate subjected to shear is examined by observing the optical effects in polarised light produced in a stressed plate of xylonite. Measurements of the shear stress at a point are obtained by using a specimen of material similar to the plate, and set along the direction of principal compression stress. A tension load is applied to this member of sufficient amount to produce a dark field at the point under examination. The intensity of tension stress so produced is twice the intensity of the shear stress in the plate. A survey of the central longitudinal section of a long rectangular plate shows that the shear stress rises very rapidly from a zero value at the ends, and reaches a maximum at a distance of rather less than the face width of the plate. As the distance from the ends increases the stress decreases slightly in value until it reaches a minimum at the centre. A similar distribution also occurs at sections parallel to the central line. As the length of the plate is diminished the maximum and minimum stresses become more pronounced, and when the ratio of length to width is in the neighbourhood of two the distribution changes in such a manner that there is a maximum at the centre.

It is shown that the distribution is approximately parabolic when the length is equal to the width of the plate, and that when the length is greater than this the approximation is less close.

The experiments show that a parabolic distribution of shear is only true within narrow limits, and that in a long rectangular section the distribution may be approximately represented by a uniform shear over the central section with a rapid fall towards the ends.

"Spectroscopic Observations: Lithium and Cesium." By Dr. P. V. BEVAN.

"Metrical Analysis of Chromosome Complexes, showing Correlation between Evolutionary Development and Chromatin Thread-widths throughout the Animal Kingdom." By Capt. C. F. U. MEEK.

Measurements of chromosomes in organisms representing the principal phyla and classes of the animal kingdom have shown that lengths appear to constitute members of a series in arithmetical progression, whereas three distinct diameters exist, *viz.*, 0.21  $\mu$  in Protozoa, and 0.42  $\mu$  and 0.83  $\mu$  in low and higher Metazoan phyla respectively. Consideration of these results has suggested the following working hypothesis:—

The chromatin granules of simplest Protozoa are a visible expression of differentiation and aggregation of specialised particles concerned with transmission of hereditary characters, and as such probably do not represent the sole bearers of hereditary in the cell. The granules become converted into rods by purely linear growth accompanying evolutionary development and greater somatic complexity, and, since the rate of growth is not the same in all chromosomes, rods of various lengths are evolved. A stage in phylogeny is later reached when a maximum rod length has been attained, such limit being imposed by spindle mechanism or other physical conditions; when this occurs, chromatin units conjugate in fours, and the normal thread-width is thus doubled. The newly formed chromosomes then segment into spheres of the same diameter, and these are prepared to enter a new course of linear growth accompanying further development. The same process is repeated when the length-limit has again been reached, and in this manner the greatest thread-width has evolved. The absence of correlation between chromosome dimen-



sions and somatic characters is explicable on such an assumption, which postulates a series of cycles in the course of phylogeny.

The heterotropic chromosome alone does not belong to the general series, and its great breadth may eventually be shown to be due to conjugation of normal rods; it is probably undergoing some process of development or disintegration, and may or may not be the determining factor in sex.

# CHEMICAL SOCIETY.

Ordinary Meeting, February 1st, 1912.

Mr. C. E. GROVES, F.R.S., in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Robert Percy Douglas, Prudential Buildings, Bolton; Elliot Alfred Evans, College of Agriculture, Holmes Chapel; Edward Percy Frankland, B.A., Ph.D., M.Sc., The Dell, Northfield, Birmingham; Walter Elmslie Hawkins, B.Sc., 86, Park Lane, Croydon; Harold John de Quetteville Lenfestey, 50, Tottenhall Road, Wolverhampton; Ambat Kesava Menon, B.A., 45, York Grove, Peckham, S.E.; George Macaulay Painter, B.Sc., Rosemeade, Thundersley, Essex; Henry Alfred Shute, B.Sc., 102, Meeting House Lane, Peckham, S.E.; Arthur Wallace, B.A., B.Sc., 1, St. Lawrence Road, Clontarf, Dublin.

Of the following papers those marked \* were read:—

\*14. "The Constituents of Commercial Chrysarobin." By FRANK TUTIN and HUBERT WILLIAM BENTLEY CLEVER.

Three samples of commercial chrysarobin and one of Araroba powder have been very fully examined. Chrysarobin was found to vary considerably in the relative proportions of its constituents, but what may be considered a typical sample had the following approximate composition:—Chrysophanic acid (5 per cent); emodin monomethyl ether (2 per cent); the anthranol of chrysophanic acid, which was described by Jowett and Potter (*Trans.*, 1902, lxxxi., 1575) under the name of "chrysarobin" (46 per cent); the anthranol of emodin monomethyl ether (a small amount); monomethyl ether of dehydroemodin-anthranol,  $C_{16}H_{12}O_4$  (18 per cent); ararobinol,  $C_{23}H_{16}O_5$  (4 per cent); and an inseparable mixture of substances, together with amorphous material (about 25 per cent). One specimen of chrysarobin was devoid of ararobinol, whilst another contained a little emodin.

The Araroba powder, in addition to the above-mentioned constituents of the chrysarobin, contained an appreciable amount of emodin, a small amount of a sugar which yielded *d*-phenylglucosazone, and traces of the higher fatty acids and a substance which appeared to be a hydrocarbon.

The "dichrysarobin" and "dichrysarobin methyl ether" described by Jowett and Potter (*loc. cit.*) have been shown to be mixtures of the anthranols of chrysophanic acid and of emodin, and the anthranol of chrysophanic acid and the monomethyl ether of dehydroemodinanthranol respectively.

\*15. "The Existence of Molecular Compounds in Solution." Part I. By HAROLD LANGTON and ALBERT ERNEST DUNSTAN.

In an endeavour to show that double salts such as astrakanite have a continued existence in solution, the authors have investigated the viscosity-concentration and viscosity-temperature curves for various solutions containing the mixed sodium and magnesium sulphates and astrakanite itself.

They find that perfectly smooth curves can be constructed, and no change in curvature obtains on passing through the transition point.

Incidentally, the authors have worked out a simple method for the determination of transition points.

16. "Researches on Bleaching Powder. Part II. The Action of Dilute Acids on Bleaching Powder." By ROBERT LLEWELLYN TAYLOR and CLIFFORD BOSTOCK.

The authors have used Taylor's method of determining the proportion of hypochlorous acid and chlorine in a mixture of the two for investigating the action of (a) sulphuric, hydrochloric, and nitric acids; (b) acetic and phosphoric acids; (c) boric and carbonic acids, on a mixture of bleaching powder and water.

When bleaching powder mixed with thirty times its weight of water is distilled with one of the three first acids, in quantity slightly greater than is required to neutralise the free lime, hypochlorous acid with a small amount of chlorine is evolved. When the acid is sufficient to decompose the whole of the hypochlorite present as well, the proportion of chlorine is greater. With larger quantities of acid the amount of hypochlorous acid rapidly diminishes until nothing but chlorine is evolved. There is not much difference in the action of the three acids.

Acetic and phosphoric acids behave much in the same way, using small quantities of acid, but even with comparatively large amounts of acid the proportion of hypochlorous acid does not fall much below 50 per cent.

When bleaching powder is distilled with once or twice its weight of boric acid and a sufficient amount of water, almost pure hypochlorous acid is obtained, and there is not much difference in the result if the boric acid used is as much as three times the weight of the bleaching powder.

When carbon dioxide is bubbled through a mixture of bleaching powder and water at different temperatures whilst at the ordinary temperature nothing but chlorine is evolved, as soon as the liquid becomes warm some hypochlorous acid is given off. As the temperature rises the proportion of hypochlorous acid increases, until, when the liquid is actively boiling, the distillate is a practically pure solution of hypochlorous acid, hardly any chlorine being evolved.

17. "The Quantitative Estimation of Hydroxy-, Amino- and Imino-derivatives of Organic Compounds by means of the Grignard Reagent, and the Nature of the Change taking place in Solution." By HAROLD HIBBERT.

The author finds that the lower fatty alcohols when treated with magnesium methyl iodide in phenetole or amyl ether solution react quite abnormally, the amount of methane evolved falling much below that demanded by theory; thus with methyl, ethyl, and propyl alcohols the methane evolved amounts to only 43, 71, and 83 per cent respectively. The lower fatty amines also behave abnormally in these solvents, in certain cases no evolution of gas whatever taking place at the ordinary temperature when such derivatives are mixed with the Grignard reagent. Experiments carried out in phenetole solution with fatty and aromatic hydroxy-, amino-, and imino-derivatives always gave too low values. The cause of this would seem to be (at least, in the case of the lower fatty alcohols) in the formation of two isomeric compounds, namely, (a)  $\text{H} > \text{O} < \begin{smallmatrix} \text{R} \\ \text{MgI} \end{smallmatrix} \text{CH}_3$  and (b)  $\text{H} > \text{O} < \begin{smallmatrix} \text{R} \\ \text{MgI} \end{smallmatrix} \text{CH}_3$ , one of

which, (a), is stable, the other, (b), unstable, decomposing at the ordinary temperature into methane and  $\text{RO} \cdot \text{MgI}$ . Evidence was given indicating that on mixing one of the lower alcohols with magnesium methyl iodide in phenetole solution, an equilibrium mixture of the above two isomeric forms is produced.

The conclusion was drawn that the method originally proposed by Hibbert and Sudborough (*Trans.*, 1904, lxxv., 933) for the estimation of hydroxyl groups in organic compounds is not generally applicable; only in the case of the aromatic derivatives and where amyl ether (not phenetole) is employed as the solvent, are the results of value. Pyridine (Zerewitinoff, *Ber.*, 1907, xl., 2023) appears accordingly to be the most suitable solvent for this purpose, but as no experiments have as yet been carried out by him on the lower fatty alcohols and amines in this

solvent, no decisive answer can as yet be given regarding this substance. The use of dimethylaniline was suggested as a possible substitute for pyridine.

18. "An Exact Investigation of the Three Component System: Sodium Oxide, Acetic Anhydride, Water." By ALFRED CHARLES DUNNINGHAM.

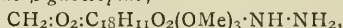
This system has been investigated fully from the point of view of the phase rule between the temperatures  $0^{\circ}$  and  $75^{\circ}$ . The author finds the only phases stable between these temperatures to have the formulæ  $C_2H_3O_2Na$ ,  $C_2H_3O_2Na, 3H_2O$ ,  $C_2H_3O_2Na, C_2H_4O_2$ , and  $C_2H_3O_2Na, 2C_2H_4O_2$ . No trace of the hemihydrate,  $C_2H_3O_2Na, \frac{1}{2}H_2O$ , has been found, although this was given by Dukelski (*Zeit. Anorg. Chem.*, 1909, lxii., 114) as the phase formed at  $30^{\circ}$  by the dehydration of  $C_2H_3O_2Na, 3H_2O$  by sodium hydroxide.

19. " $\beta$ -Gnoscopine." (Preliminary Note). By EDWARD HOPE and ROBERT ROBINSON.

The condensation of cotarnine with nitro-mecone, resulting in the production of a base,  $CH_2:O_2:C_{18}H_{11}O_2(OMe)_3 \cdot NO_2$ , has already been briefly described (Hope and Robinson, *Proc.*, 1910, xxvi., 228), and the substance so synthesised was termed nitro-gnoscopine. The amino-derivative, obtained on reduction, has now been converted into the hydrazine, which, on oxidation, yields not gnoscopine, but a stereoisomeride. It is proposed that *r*-narcotine shall be termed  $\alpha$ -gnoscopine, whilst the new stereoisomeride is  $\beta$  gnoscopine.

In consequence, the nitro- and amino-derivatives are nitro- $\beta$ -gnoscopine and amino- $\beta$ -gnoscopine respectively.

Hydrazino- $\beta$ -gnoscopine,



is prepared by the reduction of diazotised amino- $\beta$ -gnoscopine with stannous chloride in concentrated hydrochloric acid solution. It crystallises from ethyl alcohol in prisms melting at  $205-206^{\circ}$ . Copper acetate oxidises it in cold dilute acetic acid solution, and yields  $\beta$ -gnoscopine,  $CH_2:O_2:C_{18}H_{12}O_2(OMe)_3$ .

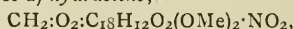
This substance crystallises in well defined prisms from methyl or ethyl alcohols, or ethyl acetate. It melts at  $180^{\circ}$ , and the melting-point is depressed when the substance is mixed with a small quantity of  $\alpha$ -gnoscopine. It forms a sparingly soluble hydrochloride and nitrate, but is in most respects similar to  $\alpha$ -gnoscopine and narcotine. On oxidation with dilute nitric acid it yields cotarnine and opianic acid. Its methosulphate is changed on boiling with dilute potassium hydroxide into the potassium salt of narceine, from which pure narceine, identical with the natural product, was isolated.

In view of the large rotation of narcotine and the pronouncedly racemic character of  $\alpha$ -gnoscopine, it is provisionally suggested that the  $\alpha$ -modification corresponds with racemic acid and the  $\beta$ -form with *i*-tartaric acid. Experiments are in progress having for their object the resolution of  $\beta$ -gnoscopine and also its conversion into  $\alpha$ -gnoscopine.

20. "Anhydrohydrastininemeconine." (Preliminary Note). By EDWARD HOPE and ROBERT ROBINSON.

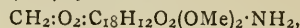
The methods employed for the synthesis of  $\beta$ -gnoscopine (see preceding abstract) have been applied to the synthesis of anhydrohydrastininemeconine [ $dl$ (or *r*)- $\beta$ (or  $\alpha$ )-hydrastine]. The various processes give excellent yields so far as the preparation of the hydrazine, and the oxidation of this compound also gives a good yield of crude material, of which only about 50 per cent is obtained in a pure condition.

Nitro- $dl$ - $\beta$ (or  $\alpha$ )-hydrastine,



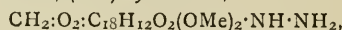
s produced by boiling an alcoholic solution of hydrastinine with nitromeconine. It crystallises from trichlorethylene in orange-yellow prisms, which melt at  $173^{\circ}$ , and decompose a few degrees higher. Its salts resemble those of nitro- $\beta$ -gnoscopine. On boiling with glacial acetic acid, hydrastinine and nitromeconine are regenerated.

Amino- $dl$ - $\beta$ (or  $\alpha$ )-hydrastine,



is readily produced by the reduction of the foregoing nitro-compound with tin and stannous chloride in glacial acetic and concentrated hydrochloric acid solution. The substance is best crystallised from chloroform and methyl alcohol, and occurs in rosette-shaped aggregates of prismatic needles. It melts at  $214^{\circ}$ , and decomposes at a slightly higher temperature. Characteristic of this substance is the very small solubility of the hydrochloride. The amine is very sparingly soluble in ether, and the solution exhibits an intense bluish violet fluorescence.

Hydrazino- $dl$ - $\beta$ (or  $\alpha$ )-hydrastine,



obtained in the usual way, crystallises from ethyl alcohol in colourless hexagonal prisms, and melts at  $174-175^{\circ}$ , with evolution of gas at  $180^{\circ}$ . On oxidation with copper acetate in faintly acid solution it is changed into anhydrohydrastininemeconine,  $CH_2:O_2:C_{18}H_{13}O_2(OMe)_2$ . This isomeride of hydrastine crystallises in apparently rectangular prisms from methyl alcohol or ethyl acetate. It melts at  $137^{\circ}$ , a fact which, combined with the known melting-points of narcotine,  $\alpha$ - and  $\beta$ -gnoscopines, and hydrastine, would seem to indicate that it is the  $\beta$ - and not the  $\alpha$ -form of inactive hydrastine. Since  $dl$ - $\alpha$ -hydrastine is an unknown substance, it is impossible to state this conclusion with confidence. The methosulphate of the synthesised base yields, on treatment with alkali, methylhydrastine, which crystallises from alcohol in yellow needles melting at  $156^{\circ}$ , and is identical with methylhydrastine derived from the natural product. These experiments are being continued and extended in various directions, and it is desired to reserve for a short period the investigation of this and similar condensations.

21. "Preparation and Properties of Sulphonic Esters." By JOHN FERNS and ARTHUR LAPWORTH.

The properties of certain sulphonic esters, as well as the question of the applicability of the methods available for the direct conversion of alcohols into sulphonic esters, have been carefully studied. These methods fail completely in certain instances, and the explanation has been found in each case.

Esters of aromatic sulphonic acids resemble the corresponding esters of the halogen hydrides, rather than those of carboxylic acids. The general character of a sulphonic ester, and consequently the most suitable method of preparing it, may often be foreseen when the properties of the corresponding halide ester are known.

The reactions of the esters with amines, potassium alkyloxide, the Grignard and other reagents have been examined in detail. The authors confirm Strecker's observation (*Ber.*, 1910, xliii., 1131 *et seq.*) that ethyl ethanesulphonate yields mainly phenyl ethyl sulphone with magnesium phenyl bromide, but they also detected ethylbenzene as a product; with ethyl toluene- $\beta$ -sulphonate, on the other hand, this reagent yields only ethylbenzene and no detectable quantity of sulphone.

22. "Menthyl Nitrilotriacetate." By PERCY FARADAY FRANKLAND and HUGH HENRY O'SULLIVAN.

In endeavouring to prepare menthyl aminoacetate by the action of ammonia on menthyl chloroacetate, the authors have obtained the menthyl ester of Heintz's nitrilotriacetic acid (*Annalen*, 1862, cxxii., 269),  $N(CH_2:CO_2:C_{10}H_{19})_3$ . It crystallises in prismatic needles melting at  $80.5^{\circ}$ . The authors have determined the rotatory power in the fused state and in methyl-alcoholic solution. The relation between the rotation of this and some other menthyl compounds was discussed.

23. "Viscosity of Aqueous Solutions of Sodium Palmitate and the Influence of Electrolytes on the same." By FREDERICK DENNY FARROW.

The viscosity has been measured, at  $70^{\circ}$ , of aqueous solutions of sodium palmitate up to concentrations 0



0.5 gm.-molecule per 1000 gms. of solution. Over this range the values found are (by interpolation on a smooth curve):—

| Concentration. | Viscosity (in absolute units $\times 10^3$ ). |
|----------------|-----------------------------------------------|
| 0.0 (water)    | 0.407                                         |
| 0.1            | 0.540                                         |
| 0.2            | 0.690                                         |
| 0.3            | 0.882                                         |
| 0.4            | 1.185                                         |
| 0.5            | 1.800                                         |

Determinations were also made of the viscosity of solutions of a definite soap concentration, in which varying amounts of sodium hydroxide, sodium chloride, or potassium chloride were present. It was found that each of these salts lowers the viscosity when present in small quantity (up to N/20 in a soap solution of concentration 0.25). The presence of these substances in larger amounts than these causes a rapid increase in the viscosity of the solution. In each of the three cases the effect of the electrolyte is quite similar, and for sodium hydroxide and sodium chloride the effects are practically identical. The bearing of this phenomenon on the colloidal nature of soap solutions was discussed.

24. "Aromatic Amino-derivatives containing Antimony." (Preliminary Note). By GILBERT T. MORGAN and FRANCIS M. G. MICKLETHWAIT.

In reference to an abstract on aromatic antimony compounds recently published by P. May (*Proc. Chem. Soc.*, xxviii., 5), the authors pointed out that they have for some time been engaged in studying the reduction products of the nitrated aromatic antimony derivatives, the orientation of which was described in a previous communication (*Trans.*, 1911, xcix., 229).

Indications were obtained of the production from *m*-nitrophenylstibinic acid of the *m*-aminophenylstibine oxide and the *m*-aminophenylstibinic acid referred to by May. Di-*m*-nitrodiphenylstibinic acid on reduction yielded di-*m*-aminodiphenylhydroxystibine,  $(\text{NH}_2 \cdot \text{C}_6\text{H}_4)_2\text{Sb} \cdot \text{OH}$ :—

0.0908 gave 0.1494  $\text{CO}_2$  and 0.0329  $\text{H}_2\text{O}$ .  $\text{C} = 44.87$ ;  $\text{H} = 4.02$ .

0.1536 gave 12.0 cc.  $\text{N}_2$  at  $17^\circ$  and 766 mm.  $\text{N} = 9.14$ .  $\text{C}_{12}\text{H}_{13}\text{ON}_2\text{Sb}$  requires  $\text{C} = 44.85$ ;  $\text{H} = 4.04$ ;  $\text{N} = 8.74$  per cent.

The base is a colourless caseous mass, melting indefinitely at  $76-80^\circ$ , precipitated from acid solutions by ammonia, and turning brown on exposure.

The hydrochloride,  $\text{SbCl}(\text{C}_6\text{H}_4 \cdot \text{NH}_2)_2 \cdot 2\text{HCl}$ , crystallises from acidified water in very soluble colourless needles:—

0.1849 gave 0.2319  $\text{CO}_2$  and 0.0628  $\text{H}_2\text{O}$ .  $\text{C} = 34.21$ ;  $\text{H} = 3.77$ .

0.1538 gave 0.1598  $\text{AgCl}$ .  $\text{Cl} = 25.71$ .  $\text{C}_{12}\text{H}_{14}\text{N}_2\text{Cl}_3\text{Sb}$  requires  $\text{C} = 34.90$ ;  $\text{H} = 3.39$ .  $\text{Cl} = 25.81$  per cent.

The base and its salts have an irritating action on the mucous membrane of the throat and nose, which is even more intense than that noticed in the case of tri-*m*-aminotriphenylstibine and its hydrochloride (*Trans.*, loc. cit.).

#### SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Annual General Meeting, February 7th, 1912.

Mr. LEONARD ARCHBUTT, President, in the Chair.

MESSRS. Shelton Gottlieb Agar, Stanley W. Bridge, Richard Victor Briggs, Francis Clifford Dyche-Teague, Francis Archibald Mason, William Bristow Saville, and George Alfred Stokes were elected members of the Society.

Certificates were read for the first time in favour of Messrs. Maurice E. Balston Buckland, Maidstone; Howard A. Caulkin, Mona Villa, Spencer Road, Belper, Derbyshire;

and Charles Reginald Wilkins, 40, Church Lane, Hornsey, London, N.

Certificates were read for the second time in favour of Miss Maud Gazdar and Mr. Herbert Hawley.

The following papers were read and discussed:—

"Determination of Butter Fat and Coconut Oil in Margarine." By F. W. F. ARNAUD and H. HAWLEY.

The formula employed by Cribb and Richards for the estimation of butter fat and coconut oil in margarine from the Reichert and Polenske values gives good results, provided coconut oil is present to the extent of about 20 per cent. If, however, less coconut oil than this be present the formula must be modified, and the authors suggest a revised formula. The amount of butter fat can also be calculated from the Kirschner value, the Polenske number being known.

"Souring of Milk." By H. DROOP RICHMOND and H. C. HUISS.

The method adopted for the determination of acidity of milk is to add 1 cc. of 0.5 per cent phenolphthalein solution in 50 per cent alcohol to 11 cc. of milk, and titrate with N/11 strontia solution till the pink tint is equal to that formed by adding 1 drop of a 0.01 rosaniline acetate solution in 96 per cent alcohol to 11 cc. of the same milk. Very concordant results are thus obtained, and all difficulties of determining the end point vanish.

If it is assumed that the rate of increase of the micro-organisms is proportional to the number present at any moment, that each micro-organism produces a unit quantity of lactic acid per unit of time, and that the rate of diffusion of the lactic from the micro-organism is much more rapid than the rate of lactic acid production, the curve expressing the rate of souring milk should be logarithmic. From the mean of a very large number of results we have plotted a curve of acidities developed against time, and find that up to the point corresponding to a development of  $45^\circ$  of acidity the agreement with a logarithmic curve is very close; at this point, which corresponds with the point at which the micro-organisms cease to increase in number, the character of the curve suddenly changes. The assumptions which may be made are these: (1) that although the micro-organisms cease to increase, they still produce a unit quantity of lactic acid per unit of time, or (2) that they produce lactic acid at a rate diminishing in proportion to the acidity produced acting for a unit of time. The first assumption would lead to a straight line, and the second to a curve of the type  $\log a = -K \log t + C$ . We find that if we take  $t$  as the time from the point where the curve changes, that our results closely correspond with the curve deduced from the second assumption. From experiments on milk to which small quantities of acid and alkali respectively have been added, we find that the rate of souring is not appreciably affected, and that the point of change of curvature takes place at that degree of acidity which corresponds with a development of  $45^\circ$  acidity in normal milk.

It is remarkable how generally constant the rate of souring of milks of different origin is, but occasionally samples of milk are met with which turn sour slower or much faster than the mean; whatever the actual rate of souring there is practically no change in the characters of the curves. There are distinct indications that the agreement of the first portion of the curve with that deduced from the assumptions may be entirely fortuitous. Thus we find that organisms cultured in milk when inoculated into milk that has been pasteurised give a rate of souring very much more rapid than they originally gave. Also a milk which has been allowed to turn slightly sour neutralised to its original acidity, and pasteurised, turns sour very much more rapidly than a fresh milk inoculated with the same organism. It is hardly reasonable to suppose that micro-organisms should be affected by the development of acidity suddenly, and only after a certain point. If we assume that the retardation of activity by the acid is balanced by a stimulation by growing in milk the curve

would remain logarithmic, and a close study of individual curves shows that this is probable, as in some of them there is distinct evidence of retardation, while others show stimulation, indicating that, though the two curves balance on the average, they do not always do so in individual cases. It follows as a corollary that the normal habitat of the organisms which cause souring in milk is not milk, but in all probability they are derived from the intestinal tract.

"A Flour Improver." By EDWARD HINKS.

Under the name of "Salox" potassium persulphate is sold as a flour improver. It is added to flour in the proportion of from  $\frac{1}{2}$  to 1 ounce to the sack. It may be detected even when in much smaller proportions than this by applying an alcoholic solution of benzidine to a paste of the flour and water; a blue colour develops round each particle of the persulphate.

## NOTICES OF BOOKS.

*The Calorific Power of Gas.* By J. H. COSTE, F.I.C., F.C.S. London: Charles Griffin and Co., Ltd. 1911. (6s. net).

In view of the increasing consumption of gas for heating purposes this book may be regarded as a timely production, which, although it is probably too technical and scientific in scope for the average gas consumer, will be very useful to gas examiners and works chemists. In it the author describes the most modern calorimetric methods of examining gas, and gives a full account of the most important legislation which has been enacted on the subject. The book contains fully illustrated descriptions of many kinds of calorimeters, with instructions for using them, and valuable citations have been taken from the "Notification of the Metropolitan Gas Referees." The book partakes more of the nature of a theoretical than a practical handbook, and as a work of reference on the principles of gas testing it is thoroughly up to date and trustworthy.

*Les Composés Chimiques dans l'Espace.* ("Chemical Compounds in Space"). By P. PALLADINO. Pavia: Premiata Tipografia Successori Fratelli Fusi. 1911.

This pamphlet is a reprint of a paper which was read before the Fifth Congress of the Società Italiana per il Progresso delle Scienze held at Rome in 1911. The author has already put forward some suggestions for calculating the form and dimensions of the combining quantities of the elements, based upon the hypothesis of the unity of matter, and in this paper he attempts to explain the chemical and physical properties of various compounds. His work displays considerable ingenuity, but his choice of formulæ, as far as can be judged from this paper, is very arbitrary, and there seems to be but little warrant for the assumptions he makes as to the various forms which the combining quantities of the elements may take.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. cliv., No. 1, January 2, 1912.

Action of Ultra-violet Rays on Sodium Hyposulphite.—Louis Marmier.—The ultra-violet rays coming from a 240 watts Westinghouse lamp were allowed to act upon solutions of sodium hyposulphite, placed at distances of 6 to 8 cm. In solutions containing less than 6 grms. per litre hydrosulphite of sodium was formed after an

exposure lasting five minutes, a deposit of sulphur being simultaneously produced. After seventy-five minutes the sodium hydrosulphite was entirely decomposed, sodium sulphite being the product. Solutions containing more than 6 grms. of sodium hyposulphite per litre did not give any hydrosulphite.

Complex Compounds of Platinous Bromide and Organic Sulphides.—Z. Tchougaff and D. Fraenkel.—When an aqueous solution of potassium bromoplatinite,  $K_2PtBr_4$  (acidified with HBr), is shaken with the theoretical amount of the disulphide,  $C_2H_5-S-CH_2-CH_2-S-C_2H_5$ , a grey crystalline substance of formula  $PtBr_2C_2H_5-S-CH_2-CH_2-S-C_2H_5$  is obtained. From its reactions with  $(Pt_4NH_3)Br_2$  it appears to be the bromoplatinite of the complex base,  $[Pt_2(C_2H_5-S-CH_2-CH_2-S-C_2H_5)](OH)_2$ . This conclusion can be confirmed synthetically.

## MISCELLANEOUS.

Moissan Memorial Lecture.—An Extra Meeting of the Chemical Society will be held on Thursday, February 29, 1912, at 8.30 p.m., when the Moissan Memorial Lecture will be delivered by Sir William Ramsay, K.C.B., F.R.S.

Royal Institution.—On Tuesday next, February 27th, at 3 o'clock, Prof. E. G. Coker will begin a course of two lectures at the Royal Institution on "Optical Determination of Stress, and some Applications to Engineering Problems"; and on Thursday, February 29th, Prof. Charles Oman will commence a course of three lectures on "Wellington's Army." The Friday Evening Discourse on March 1st will be delivered by Dr. W. J. S. Lockyer, on "The Total Solar Eclipse in the South Pacific, April, 1911"; and on March 8th by Dr. A. W. Ward, on "The Effects of the Thirty Years' War."

## NOTES AND QUERIES.

\* \* Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

Purifying Mercury in the Laboratory.—In reply to Mr. Weldon Hanson (CHEMICAL NEWS, cv., p. 46), he can get Dr. Palmaer's funnel for purifying mercury at many dealers on the Continent. In Switzerland I have obtained it at Werthemann, Botty, and Co., Hebelstrasse 5, Basel; one can find it also at Dr. Bender and Dr. Hobein, Riedstr. 15, Zurich. It costs 8.50 fr. (= nearly 6s. rod.). At Hausmann's A.-G., St. Gallen, Switzerland, Abteilung V.F.L., its cost is somewhat lower, 6 M. (= 6s.).—TAD. ESTREICHER, Laboratoire de Chimie No. 11, Université de Fribourg, Switzerland.

## MEETINGS FOR THE WEEK.

MONDAY, 26th.—Royal Society of Arts, 8. (Cantor Lecture). "The Loom and Spindle—Past, Present, and Future," by Luther Hooper.

TUESDAY, 27th.—Royal Institution, 3. "Optical Determination of Stress, and some Applications to Engineering Problems," by Prof. E. G. Coker, F.R.S.E., &c.

WEDNESDAY, 28th.—Royal Society of Arts, 8. "Education in Science as a Preparation for Industrial Work," by H. A. Roberts, M.A.

THURSDAY, 29th.—Royal Institution, 3. "Wellington's Army," by Prof. Charles Oman, M.A., &c.

Royal Society. "Bacterial Production of Acetyl-methylcarbinol and 2, 3-Butylene Glycol," by A. Harden and Dorothy Norris. "Instrument for Measuring the Distance between the Centres of Rotation of the two Eyes," by H. S. Ryland and B. T. Lang. "Locomotor Function of the Lantern in *Echinus*, with Remarks on other Allied Lantern Activities," by J. F. Gemmill. "Relation of Wild Animals to Trypanosomiasis," by Capt. A. D. Fraser and H. L. Duke. "The Transmission of *Trypanosoma nanum* (Laveran)," by H. L. Duke. "Development of a Leucocytozoon of Guinea-pigs," by E. H. Ross.

FRIDAY, March 1st.—Royal Institution, 9. "The Total Solar Eclipse in the South Pacific, April, 1911," by William J. S. Lockyer, M.A., &c.

SATURDAY, 2nd.—Royal Institution, 3. "Molecular Physics," by Sir J. J. Thomson, F.R.S., &c.



# THE CHEMICAL NEWS.

VOL. CV., No. 2727.

## THE BAKING QUALITIES OF FLOUR,\*

AS INFLUENCED BY CERTAIN CHEMICAL SUBSTANCES,  
MILLING BY-PRODUCTS, AND GERMINATION OF THE WHEAT.

By J. T. WILLARD and C. O. SWANSON.

THE milling tests of wheat and baking tests of flour conducted by the department of chemistry began in 1905, when an experimental reduction mill was purchased. During that year Mr. W. E. Mathewson, in a research conducted as a part of his work for the master's degree, made very careful analyses of several flours, including determinations of the percentages of each of the distinct proteins present, and compared their chemical composition with their baking qualities as shown by baking tests made for us in the department of domestic science. At that time the statement was frequently made, and perhaps is, even to-day, that the ratio of the gliadin to the glutenin of the flour determines its baking qualities. Mr. Mathewson's results threw grave doubt on this supposition, and all subsequent investigations in the department have confirmed the view suggested at that time, namely, that the chemical factors entering into the baking quality of flour are more complex than that. Flours may be very good in their content of gliadin and in the gliadin-glutenin ratio, and yet be inferior in baking qualities to others with supposedly less favourable composition. Of two flours essentially the same in respect to these data, one may be very good and the other very poor.

As a result of such observations the department has been conducting numerous experiments designed to throw light on the subject of baking quality in flour. Many of these do not come within the scope of the present paper, which is concerned with the effects of the addition of certain substances to the flour. These tests were suggested by the thought that, inasmuch as considerable differences in respect to the gliadin and the gliadin-glutenin ratio did not in themselves appear to influence the results much, it might easily be true that the difference in baking qualities exhibited might be caused by substances present in very small amounts. It will be recalled that capacity to produce a good loaf depends on the quality of the gluten that a given flour can yield, other conditions being favourable. Gluten does not exist as such in the flour, but is produced, in a manner not altogether understood, from constituents existing in the flour, chiefly the gliadin and the glutenin, when the flour is stirred with water.

Gliadin is a gluey adhesive substance which binds the glutenin and other constituents of the flour together in the dough and produces the well known condition so essential to the production of good bread, in which the carbon dioxide produced by yeast is held in small bubbles that give the loaf its lightness. If the gluten is too weak the partitions between the globules are broken, and globules coalesce, with the production of coarse-grained bread. A weak gluten will yield under the weight of the loaf, and, instead of rising in a well-rounded form, will flatten out and run over the edge of the pan, if possible. The production of a good loaf depends on the physical properties of the gluten. It is well known that small percentages of substances may cause very great differences in the physical properties of mixtures. It is, therefore, quite reasonable to expect that the physical properties of gluten may be profoundly affected by small quantities of associated substances. This would be a purely physical phenomenon. It is, however, also possible that small quantities of sub-

stances may influence the character of the loaf in an entirely different manner, by favouring or inhibiting, as the case may be, the growth of the yeast.

It is well known that graham flour lacks the power to yield as round and light a loaf as does white flour produced from the same wheat. This fact suggested experiments to ascertain the effect of substances in the bran and shorts the action of which is excluded from white flour. These effects were tested in different ways, which will be detailed later, using bran, extracted bran, extract from bran, extract from wheat scorings, &c.

Recent research has shown that the protein substances consist in large part of nuclei derived from a considerable number of amino acids. It is highly probable that, in the growth of the yeast in the flour, hydrolysis of the proteins takes place with the liberation of some of these amino acids, and it is possible that they play an important part in the development of the yeast, or affect the physical properties of the gluten. A part of our study in this connection, then, has been to ascertain what effect, if any, the addition of small amounts of amino acids has on the character of the loaf produced. As but few of the amino acids represented in proteins are to be purchased in the market, our experiments in this line are not completed as yet. It is planned to import as complete a list of these substances as can be obtained for continuation of this investigation.

A considerable number of observations are made in connection with each baking test, and a detailed study of any set of these would involve considerable time and the inspection of many figures—a proceeding that would be wearisome to all not especially interested in this line of work. In most cases, therefore, only the figures for loaf volume are presented.

In addition to the experiments using amino acids, others have been made with salts such as might be present in the flour or that are related to them.

The accompanying table exhibits the results obtained with bran, &c. If bran were merely a diluent, and without active effect on the gluten, we should expect that the quality of the loaf would be affected by incorporating a considerable percentage of it with the flour. To offset this effect of dilution a loaf was made in which an equal weight of starch was used instead of bran, starch being presumed to be without specific influence, or, at least, without much influence except as a diluent. In all of our baking tests a check loaf is baked from the untreated standard flour, and with this, as a rule, all others are to be compared. The difficulty of conducting exactly comparable baking tests is such that, without such a test loaf produced by a parallel treatment in each baking, it would be impossible to draw any conclusions. Of the results obtained with the bran, in addition to loaf volume, there is presented the scoring as to texture, and total time in minutes required for the rising.

The bran used in these tests was free from scorings or screenings of any kind. In preparing the extracts, 500 grms. were treated with 2000 cc. of water. The bran was allowed to soak over night, and then placed on linen and the extract squeezed out. The residue was treated several times with additional portions of water in preparing the washed bran. In extracting hot, the bran was boiled about ten minutes with water, then washed several times on linen with hot water, the water being squeezed out.

Table I. shows that the unextracted bran had a notable deteriorating effect on the loaf, in respect to both volume and texture, as compared with the check loaf or with the loaf to which an equal weight of starch was added. The extracted bran was less marked in its effect on loaf texture, and the loaf volume exceeded that of the loaf in which starch was used. The loaf in which the extract from 40 grms. of bran was used was the best of all. The fact that extracted bran and bran extract each produces better results than when the two coexist in the unextracted bran is something that would not have been expected, but which was confirmed by the repetition of the test.

\* Abstract of a Paper read before the Kansas Academy of Sciences.

TABLE I.—*Effect of Bran, Bran Extract, and Starch.*

|                                           | Time for total rise (mins.). |     | Loaf volume. |      | Loaf texture (100=perfection). |     |
|-------------------------------------------|------------------------------|-----|--------------|------|--------------------------------|-----|
|                                           | I.                           | II. | I.           | II.  | I.                             | II. |
| Check .. .. .                             | 173                          | 162 | 1430         | 1410 | 95                             | 95  |
| Starch, 40 grms. .. .                     | 168                          | 159 | 1290         | 1290 | 95                             | 95  |
| Bran, 40 grms. .. .                       | 154                          | 143 | 1260         | 1250 | 91                             | 91  |
| Bran, extracted by cold water, 40 grms. . | 148                          | 137 | 1380         | 1370 | 92                             | 92  |
| Bran, extracted by hot water, 40 grms. .  | 142                          | 137 | 1300         | 1310 | 92                             | 92  |
| Extract from 40 grms. bran, cold water. . | 136                          | 127 | 1520         | 1540 | 96                             | 96  |

TABLE II.—*Loaf Volume as Affected by different Substances.*

| Substance added.                                                                                        | Minimum amount (grms.). | Times minimum amount. |      |      |      |      |      |
|---------------------------------------------------------------------------------------------------------|-------------------------|-----------------------|------|------|------|------|------|
|                                                                                                         |                         | 0.                    | 1.   | 2.   | 4.   | 8.   | 16.  |
| Bran extract, cold extraction .. .                                                                      | 2.5 (a)                 | 1480                  | 1490 | 1410 | 1510 | 1520 | 1520 |
| Bran extract, cold extraction, filtered .. .                                                            | 2.5 (a)                 | 1470                  | 1500 | 1520 | 1550 | 1550 | 1550 |
| Bran extract, hot extraction .. .                                                                       | 2.5 (a)                 | 1400                  | 1420 | 1440 | 1520 | 1550 | 1560 |
| Wheat scourings, Extract I. .. .                                                                        | 2.5 (a)                 | 1450                  | 1480 | 1500 | 1520 | 1540 | 1490 |
| Wheat scourings, Extract II. .. .                                                                       | 2.5 (a)                 | 1360                  | 1460 | 1280 | 1360 | 1260 | 1190 |
| Peptones .. .                                                                                           | 0.4                     | 1380                  | 1390 | 1370 | 1280 | 1300 | 1320 |
| Glycocoll, CH <sub>2</sub> (NH <sub>2</sub> ).COOH .. .                                                 | 0.1                     | 1380                  | 1330 | 1270 | 1240 | 1180 | 1180 |
| Leucin, (CH <sub>3</sub> ) <sub>2</sub> CH.CH <sub>2</sub> (NH <sub>2</sub> ).CH <sub>2</sub> COOH .. . | 0.025                   | 1380                  | 1340 | 1280 | 1270 | 1360 | 1330 |
| Aspartic acid, COOH.CH <sub>2</sub> CH(NH <sub>2</sub> ).COOH .. .                                      | 0.1                     | 1460                  | 1470 | 1460 | 1420 | 1500 | 1530 |
| Asparagin, CONH <sub>2</sub> .CH <sub>2</sub> CH(NH <sub>2</sub> ).COOH + H <sub>2</sub> O .. .         | 0.1                     | 1440                  | 1410 | 1380 | 1380 | 1300 | 1370 |
| Ammonium acetate, CH <sub>3</sub> .COONH <sub>4</sub> .. .                                              | 0.1                     | 1440                  | 1490 | 1490 | 1500 | 1520 | 1500 |
| Ammonium tartrate, NH <sub>4</sub> OOCCO.HOCH <sub>2</sub> COONH <sub>4</sub> .. .                      | 0.1                     | 1460                  | 1470 | 1450 | 1520 | 1550 | 1400 |
| Ammonium chloride, NH <sub>4</sub> Cl .. .                                                              | 0.025                   | 1300                  | 1420 | 1260 | 1520 | 1600 | 1610 |
| Ammonium phosphate, (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> .. .                               | 0.1                     | 1470                  | 1470 | 1470 | 1470 | 1440 | 1430 |
| Sodium phosphate, Na <sub>2</sub> HPO <sub>4</sub> .. .                                                 | 0.4                     | 1430                  | 1450 | 1460 | 1400 | 1410 | 1420 |
| Sodium bicarbonate, NaHCO <sub>3</sub> .. .                                                             | 0.1                     | 1330                  | 1370 | 1350 | 1210 | 1170 | 1170 |
| Sodium formate, H.COONa .. .                                                                            | 0.1                     | 1550                  | 1530 | 1500 | 1470 | 1550 | 1500 |
| Potassium nitrate, KNO <sub>3</sub> .. .                                                                | 0.1                     | 1500                  | 1480 | 1440 | 1500 | 1520 | 1520 |

(a) These figures show the weights of material extracted.

TABLE III.—*Baking Test on Flour from Germinated Wheat.*

| No. | Loss in germination and drying. | Loss in scouring. | Per cent total loss. | Per cent of moisture. | Per cent of absorption. | Time of rising. | Weight of baked loaf (grms.). | Volume of loaf (cub. ins.). | Per cent gliadin is of protein— | Amino-nitrogen × 6.25. |
|-----|---------------------------------|-------------------|----------------------|-----------------------|-------------------------|-----------------|-------------------------------|-----------------------------|---------------------------------|------------------------|
| 1.  | 83                              | 75                | 5.5                  | 11.07                 | 59.2                    | 1 : 52          | 515                           | 83                          | 52.4                            | 0.136                  |
| 2.  | 43                              | 86                | 4.3                  | 12.00                 | 52.5                    | 2 : 13          | 509                           | 88                          | 52.7                            | 0.144                  |
| 3.  | 100                             | 80                | 6.3                  | 11.37                 | 50.8                    | 2 : 03          | 504                           | 93                          | 55.8                            | 0.184                  |
| 4.  | 149                             | 200               | 11.6                 | 11.67                 | 49.17                   | 2 : 17          | 498                           | 84                          | 55.8                            | 0.247                  |
| 5.  | 250                             | 452               | 23.4                 | 10.65                 | 47.5                    | 2 : 55          | 492                           | 84                          | 56.5                            | 0.351                  |
| 6.  | 54                              | 52                | 3.5                  | 11.55                 | 54.2                    | 1 : 58          | 515                           | 97                          | 50.7                            | 0.192                  |
| 7.  | 160                             | 63                | 7.4                  | 8.50                  | 56.67                   | 2 : 25          | 524                           | 69                          | 43.4                            | 0.512                  |
| 8.  | 0                               | 23                | 1.6                  | 11.71                 | 56.67                   | 1 : 25          | 524                           | 85                          | 48.4                            | 0.128                  |

Table II. gives data concerning the effect of various substances on loaf volume. Bran extracts were used in quantities obtained from weights of bran in geometrical ratio. The larger amounts produced greater effects in the same direction. In the case of the loaf with which extract prepared with hot water was used, the largest amount caused a poorer texture of loaf, and with the other two cases the deteriorating effect of the increased quantities was manifested when the extract was used in still less amounts.

The effects of extracts derived from wheat scourings are, on the whole, undesirable, though in respect to loaf volume this does not appear in one of the trials. The doughs produced were sticky and undesirable, and the effects were more pronounced with the larger quantities of extract.

When peptones were added to the flour in amounts of from 0.1 gm. to 1.0 gm. but little effect was observed, but with larger quantities they were deleterious to the texture and loaf volume. Their most marked effect was in producing a notable stickiness in the dough. Peptones were tried because of their relation to proteids and amino acids, being intermediate in chemical complexity and structure.

Glycocoll was very pronounced in its effects, producing

a dough that was sticky, runny, and stringy. It would stretch out like toffy, but lacked in elasticity. It resembled the dough produced from flour made from badly germinated wheat. The loaf volume was distinctly reduced and the texture impaired.

The effects of leucin were similar to those of glycocoll, but not so pronounced. It caused, however, the development of a very disagreeable odour.

Aspartic acid did not have any very great effect, but such as was produced was beneficial rather than otherwise.

Asparagin, however—the amide of aspartic acid—was injurious in its effects. While it caused a shortening of the time of rising, probably by a stimulation of the growth of the yeast, it weakened the gluten, thus decreasing the oven expansion and loaf volume. Similar effects are observed with flour from germinated wheat, and asparagin is well known as one of the products of the proteid metabolism accompanying germination.

Of the ammonium salts tried, ammonium chloride had so marked an effect that the quantities used were cut down to a minimum of 0.025 gm. This amount and up to sixteen times as much, at least, had a most pronounced beneficial effect on the texture and loaf volume. The salt apparently assists the growth of the yeast, as the period of



rising is shortened. Ammonium acetate has a similar but much less marked effect. In the larger amounts, however, it impaired the quality of the loaf in respect to texture. Ammonium tartrate had a very slight effect, and the same is true of ammonium phosphate. In the latter case the results upon the six loaves might almost be taken as an example of concordance of parallel uniform tests.

Sodium bicarbonate was distinctly detrimental in its effects, increasing the time of rising and diminishing the volume of the loaf. Sodium phosphate, sodium formate, and potassium nitrate do not call for any special comment at this time.

On the whole, it is evident that chemical substances in many cases have distinct, and in some cases very pronounced, effects upon the baking qualities of flour, and it is believed that a field has been opened that will repay further working. It is highly probable that the differences in the baking quality of flours are due to small differences in their content of these and similar substances as much as to their differences in composition in respect to the chief constituents.

Considerable study has been made of the effects of germination of wheat upon the baking qualities of flour produced from it, and the effect of such flour when mixed with flour from sound wheat. As germination produces amino-compounds, it was to be expected that somewhat similar results would be obtained with flour made from germinated wheat as with flour to which amino-compounds had been added. This was found to be the case. Table III. shows part of the results obtained in this connection. No. 8 is the check, and shows the results obtained with sound wheat. Nos. 1, 6, and 7 were germinated one day; No. 2, two days; No. 3, three days; No. 4, four days; and No. 5, five days. In the germination the wheat was placed between layers of cheese-cloth on a bed of wet sand, the whole being sprinkled four times a day. All of the samples but No. 6 were covered by muslin bags which had been soaked in a solution of formaldehyde. This was for the purpose of preventing mould. All of the germinated samples excepting No. 7 were spread out on a cloth on the floor to dry. No. 7 was dried for two days in a steam-oven instead of on the floor. The weather was warm, and two days' exposure to conditions for germination gave results that were readily perceptible to the eye. The table shows the more interesting data obtained. Up to the third but little effect on the baking quality was observed. After that the loss on germination became very noticeable, and the quality of the bread deteriorated. While the loaf volume was increased for the first three days, after that it dropped back, and accompanying this there was a noticeable deterioration in the texture of the crumb. In the case of No. 7, which was dried by steam-heat, a very serious injury to the flour was observed. This is shown in part by the small loaf volume. The texture of the loaf was very poor, and the alcohol-soluble protein considerably diminished.

In a second series of experiments baking tests were made with standard flour, and with flour made from badly germinated wheat, and with various mixtures of the two. The deleterious influence of the flour from the germinated wheat was strongly manifested even when only one-thirtieth of the mixture was flour from such wheat. With larger amounts the product showed that the mixtures were wholly unfit for bread making. The evil effects of mixing wheat damaged by germination with sound wheat was brought out for the first time by these experiments. Such wheat may be manipulated so that when mixed in small quantities with sound wheat it can scarcely be detected.

South-Western Polytechnic Institute, Chelsea.—Sir David Gill, K.C.B., F.R.S., presents prizes and certificates to students of Evening Classes and Day College on March 15th at 8 o'clock p.m. Laboratories and Workshops open to public inspection at 9.15 p.m.

## ANALYSIS OF PINEAPPLE (*ANANAS SATIVUS*).

By E. V. FLACK, Government Analyst.

THE following are the results of the analyses of pineapple (fruit and plant) grown in the Bathurst District of the Cape, together with the analysis of a sample of the piny soil:—

Bathurst is a district which exports considerable quantities of pines to the English market. The pines were grown on a sandy loam overlying gravel. The piny is a good cropper, from seven to nine years old, and yields six to eight pines per bush per annum of an average weight per pine of 1½ lbs. In the acre are roughly 2400 plants, of an average weight of 66 lbs. 9 ozs.

|                         | Fresh fruit (per cent). | Fresh plant (per cent) |
|-------------------------|-------------------------|------------------------|
| Moisture .. .. .        | 83.86                   | 81.45                  |
| Crude fat .. .. .       | 1.11                    | 0.47                   |
| Proteins .. .. .        | 0.49                    | 0.75                   |
| Crude fibre .. .. .     | 0.33                    | 3.25                   |
| Nitrogen-free extract.. | 13.51                   | 12.02                  |
| Ash .. .. .             | 0.70                    | 2.06                   |
| Silica .. .. .          | 0.069                   | 1.12                   |
| Lime .. .. .            | 0.047                   | 0.121                  |
| Potash .. .. .          | 0.358                   | 0.356                  |
| Phosphoric oxide ..     | 0.024                   | 0.029                  |

The soil analysed as follows:—

| On 1 mm. Product.                            |  | Per cent. |
|----------------------------------------------|--|-----------|
| Nitrogen .. .. .                             |  | 0.126     |
| On ½ mm. Product. Hydrochloric Acid Extract. |  |           |
| Specific Gravity 1.115.                      |  |           |
| Lime .. .. .                                 |  | 0.086     |
| Potash .. .. .                               |  | 0.062     |
| Phosphoric oxide ..                          |  | 0.050     |

| On 3 mm. Product. Dyer's 1 per cent Citric Acid Extract. |  |       |
|----------------------------------------------------------|--|-------|
| Potash .. .. .                                           |  | 0.005 |
| Phosphoric oxide ..                                      |  | 0.010 |

Government Analytical Laboratory,  
Grahamstown, January 29, 1912.

## THE SULPHURIC ACID-SULPHATE BATH FOR MELTING-POINT DETERMINATIONS.

By HEYWARD SCUDDER.

THIS bath, made by boiling a mixture by weight of concentrated sulphuric acid and (a) 30 per cent of potassium sulphate for temperatures up to 325°, or (b) 40 per cent of potassium sulphate for temperatures up to 365°, has received some adverse criticism in the last few years because the limitations of its use have not been considered.

In the original description (*Journ. Am. Chem. Soc.*, 1903, xxv., 161) it is distinctly stated that it is impossible to use such mixtures in an open beaker for temperatures as high as these without having disagreeable amounts of acid vapour given off. This vapour will attack cork held a short distance above the beaker. The same objection holds to any form of apparatus in which a short wide tube is used. The apparatus as described consists of a round bottom 150—200 cc. flask, with a test-tube inserted so that the bottom of the tube is about 1 cm. from the bottom of the flask (such a tube will hang from the lip of the flask), both tube and flask containing the bath. In the description of this apparatus given by Mulliken (*Identification of Pure Organic Compounds*, vol. i., 1904) the diameter of the tube is given as about 1.5 cm., the length about 13 cm. In such an apparatus rubber bands placed at a height of about 2 cm. above the level of the bath may be used to hold the capillary tube to the thermometer. The

convenience of using rubber bands instead of platinum wire is great, especially if many melting-points are taken.

The form (a) remains liquid at ordinary temperatures, the form (b) becomes a soft mass when cold. Both forms may solidify to a hard mass. This solidification occurs occasionally, and there is no way to avoid it. In the apparatus described it does not occur often enough to be troublesome. In open beakers it occurs more often. The mass can be melted and the bath used as before. The solidification is evidently due to the crystallisation of a compound existing in a state of supersaturation, for it can be produced by inoculating a cold liquid bath with a small piece of the solid substance, the solidification being accompanied by a rise of temperature. As in all cases of supersaturated solutions, if one is working for some time in one room with these solutions, it becomes difficult to keep them in open vessels, since the dust on the shelves and walls will gradually accumulate a certain amount of the solid, sufficient to set up crystallisation if it comes in contact with the solution. This contact with dust does not explain the solidification that occurs in the flask of the apparatus described. I have made many experiments but have never been able to discover the conditions necessary to produce solidification when the inside of the flask is kept moderately clean (inoculation being excluded).

Breaking of the flask may occur with form (b), if solidification takes place. In my own experience this does not occur as often as when paraffin, &c., are used. With form (a) breakage ought not to occur more often than it does with any flask that is repeatedly heated and cooled rather rapidly. But after a number of years experience with chemical glassware, after seeing beakers fall 4 or 5 feet on to a cement floor with no injury at all, while other beakers crack when gently placed on a desk, I am willing to accept any statement about the breakage of glass, even the one most commonly met with in domestic experience, that "It fell to pieces while I was holding it in my hand."

While the convenience of taking melting-points in capillary tubes is universally admitted, the accuracy of the method has been under estimated since the investigation of Landolt (*Zeit. Phys. Chem.*, 1889, iv., 349). But Wegscheider (*Chem. Zeit.*, 1905, xxix., 1224) has shown by experiments of his own, confirmed by those of others, that in the case of pure compounds not decomposed by heat (and of course the method of Landolt can not be used except in the case of such compounds), it is possible to get results accurate to tenths of a degree by heating only a few tenths of a degree a minute, when within 10° to 20° of the melting-point. Landolt heated at the rate of 2° a minute, when using a capillary. Wegscheider further points out that since most compounds are only fairly pure they are actually mixtures of variable composition, so that their behaviour when melting may give indications of value in estimating the amount or kind of impurity. The impurity may melt at a temperature above or below that of the main compound, and after the beginning of melting there may be a eutectic, or a eutectic containing the impurity or main compound still undissolved for a noticeable length of time. For this reason the use of a bath which allows observation of the capillary is better than the use of electrical devices or the Maquenne block, and for the same reason the temperature at the beginning of melting and when the whole is liquid should be given. He further points out that if a compound is drawn into a capillary in a molten state, then cooled and the melting-point taken, in addition to the danger of decomposition from heat, there is the possibility of error from the existence of a polymorph, since the first heating may have transformed the compound in whole or in part into a polymorph with a different melting-point. The same objection would hold against the practice of taking a melting-point, allowing the compound to solidify in the capillary, and then taking the melting-point again.

## ON THE ALKYLATION OF ACID AMIDES.

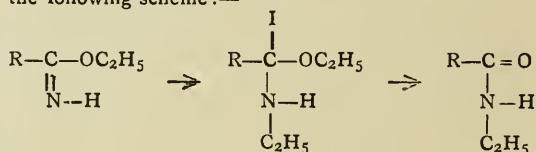
By MOTOOKI MATSUI.

It is generally known that a compound having the atomic

—C=O  
group —N—H frequently behaves as a compound of enolic

form. Now since acid amides and anilides contain such an atomic group, it may be anticipated that they will react with the enolic form under suitable conditions. Nevertheless, facts which support this anticipation are rather wanting, compounds of this class hitherto known to have enolic form being their silver salts only. Not only such facts were insufficient, but almost all the investigations carried out in this direction have tended to disprove this view (Kieseritsky, *Zeit. Phys. Chem.*, 1899, xxviii., 385; Ley u. Kissel, *Ber.*, 1899, xxxii., 1357; Titherley, *Journ. Chem. Soc.*, 1901, lxxix., 391).

In his previous communication the author has stated, that amides change directly and easily into imino-esters by the action of dimethyl sulphate, and that this reaction may be regarded as a support for the imino-hydrine formula of amides (*Memoirs of the College of Science*, &c., 1909, ii., 37). Now the author was led to the thought, that if amides really act upon dimethyl sulphate as imino-hydrines, it would not be improbable to expect their action toward other alkylating agents, such as alkyl iodide, to proceed similarly. According to the experiments carried out by Wheeler and Johnson (*Am. Chem. Journ.*, 1899, xxi., 185) imino-esters combine with alkyl iodide and pass into alkyl amides at 100°, as is represented by the following scheme:—



Therefore in order to prepare imino-esters from amides and alkyl iodide the temperature of the reaction must be kept below 100°. But at the ordinary temperature the interaction of these two substances is hardly perceptible. So that we have to seek some means to effect the alkylation at the ordinary temperature.

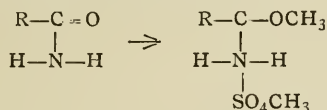
Use of silver oxide along with halogen alkyl in alkylation has been tried by many investigators and always gave good results (Purdie and Pitkeathly, *Journ. Chem. Soc.*, 1899, lxxvi., 257; Purdie and Irvine, *Ibid.*, 1899, lxxv., 485; McKenzie, *Ibid.*, 1899, lxxv., 754; Lander, *Ibid.*, 1900, lxxvii., 729). Indeed, Lander (*loc. cit.*) applied this method on the alkylation of benzamide, and obtained benzimino-ester as the product. He, however, considered it inadequate to regard the silver oxide merely as an agent for removing the elements of hydrogen iodide from the sphere of action, but he assumed the intermediate production of silver derivative which by double decomposition with alkyl iodide yields the corresponding ether. The fact that other oxides, such as those of lead, copper, and zinc, are incapable of replacing oxide of silver in the reaction, was conceived by him to be well in harmony with his view. But according to the author's experiments cuprous oxide and lead oxide are both capable of replacing silver oxide in alkylation, and even anhydrous potassium carbonate acts similarly to bring about the reaction between amides and alkyl iodide. From these experimental results it seems highly probable that silver oxide used in alkylation simply acts to accelerate the reaction between amides and alkyl iodide, whose interaction does, otherwise, occur only at a high temperature. If this view be correct, it may be concluded that alkylation of acid amides always proceeds in one direction, independent of the nature of the alkylating agents, and results in imino-esters, whether dimethyl sulphate or alkyl iodide be used, and this conclusion suggests



the existence of imino-hydrines as the tautomer of acid amides.

The experiments have been conducted in the following way:—In a flask provided with a reflux condenser benzamide or acetamide was mixed together with an excess of ethyl iodide, and some cuprous oxide, lead oxide, or anhydrous potassium carbonate was added. The mixture was heated in a water-bath for three or four hours, and after the heating was over the contents of the flask were cooled and extracted with ether. In the case of acetamide the ethereal solution was fractionated, and the portion distilling at 60–70° was found to contain acetiminoethyl ester, which was confirmed by its characteristic smell, by its alkaline reaction, and by the decomposition product of its hydrochloride; in the case of benzamide the ethereal solution was saturated with dry hydrogen chloride, and benziminoethyl ester was isolated as its hydrochloride and examined.

After the previous communication (*Memoirs of the College of Science, &c.*, 1909, ii., 37) had been published it was found that the author had unfortunately overlooked Bühner's work on alkylation of amides with dimethyl sulphate (*Ann. Chem.*, 1904, cccxxxiii., 289). Bühner interpreted this reaction, however, to have been caused by the addition of dimethyl sulphate in 1.3-positions of the ketonic form of amides, but not by the simple substitution of enolic hydrogen with methyl group, thus:—



If this view be granted, alkylation of thiamides with the same alkylating agent described in my previous communication (*loc. cit.*) must also be regarded as having been brought about by the addition of dimethyl sulphate on thiamides, to which the usual ketonic formula should, so far, be assigned as the consequence. But since the fact that thiamides behave very frequently as thioimino-acids is indisputable, it seems to the author more probable to explain the reaction as simple alkylation of thioimino-acids than to regard it as an addition of dimethyl sulphate

$\text{R}-\text{C}=\text{S}$  in 1.3-positions of  $\text{H}-\text{N}-\text{H}$ . If so, the transformation of ordinary amides into imino-esters by alkylation might analogously be explained by assigning the imino-hydrine formula for amides.—*Memoirs of the College of Science and Engineering, Kyoto Imperial University*, ii., No. 13.

## CUPFERRON:

### ITS USE IN QUANTITATIVE ANALYSIS.

By OSKAR BAUDISCH and VICTOR L. KING.

UNDER the name "Cupferron" one of us (Baudisch) introduced the ammonium salt of nitrosophenylhydroxylamine,  $\text{C}_6\text{H}_5(\text{NO})\text{ONH}_4$ , into quantitative analysis as a precipitant for cupric and ferric ions. By means of cupferron, iron and copper may be separated very rapidly and exactly, not only from one another but also from almost all the other metals. The new method exceeds in elegance, simplicity, and rapidity of operation all the methods known up to the present time for the separation of iron and copper, and has already met with great favour in technical chemical analysis in factories and mining and metallurgical plants.

The advantages of precipitating with cupferron are as follows:—

1. Iron and copper are precipitated from solutions strongly acid either with mineral or acetic acids. The precipitated iron and copper salts may be very easily and

thoroughly washed free from the chlorides, nitrates, sulphates, &c., of any other metals which may be in solution.

2. The precipitates settle rapidly, and may be filtered off without loss of time.

3. The separation of the iron from the copper is accomplished simply by washing the precipitate on the filter with dilute ammonium hydroxide solution. The ferric salt is completely insoluble and remains on the filter.

4. The iron salt is readily soluble in ether, chloroform, acetone, &c., and may be dissolved, on the filter, away from any other metallic salts such as Pb, Ag, Hg, Sn salts, which may have been simultaneously precipitated.

The particular value of the new method lies in the fact that by its means iron may be rapidly separated from aluminium, manganese, chromium, nickel, and cobalt. The "cupferron" method has been thoroughly tested from many sides, and the work of H. Nissenson, A. Biltz and O. Hödthe, and Fresenius quite confirm our results.

Cupferron will undoubtedly find extensive application in the quantitative analysis of widely different materials, for it has also been discovered that titanium, cerium, and zirconium may be quantitatively precipitated from acid solutions by it.

An example showing the application of the method to a manganese ore may be of value.

Dissolve 5.0 grms. of the finely pulverised ore in 60 cc. of conc. HCl, oxidise the iron with  $\text{KClO}_3$ , and after expelling the chlorine, dilute to 500 cc. with water. Pipette out 25 cc. into a beaker, and add 20 cc. conc. HCl and 100 cc. cold distilled water. Allow a solution of about 3.0 grms. of cupferron in 50 cc. of cold water to flow in a fine stream down the side of the beaker, with constant stirring. A brownish red, partly amorphous, partly crystalline precipitate separates out. As soon as a drop of the reagent causes the formation of a snow-white crystalline precipitate, all the iron is down. For certainty's sake add an excess of the reagent, stir well, and filter off with suction. In case the last particles of the precipitate cling tenaciously to the beaker, add a little ether to loosen them, and then remove the ether by adding a little boiling water. In this manner it is possible to quantitatively transfer the precipitate to the filter. The precipitate is now washed with cold water until the filtrate is no longer acid with the mineral acid used. Manganese may be determined in the filtrate. The precipitate is now washed twice with dilute ammonia (1 vol. conc.  $\text{NH}_4\text{OH}$  to 1 vol.  $\text{H}_2\text{O}$ ) in order to remove the excess of reagent. Wash once more with cold water, and fold the wet paper and precipitate together and dry in a weighed platinum or porcelain crucible with a small flame. Then cover the crucible, and heat until no more inflammable gases are evolved, and then ignite to  $\text{Fe}_2\text{O}_3$ , cool, and weigh.

1. Substance 5.0 grms. 25/500 = 1/20 taken  $\text{Fe}_2\text{O}_3$   
0.0330 = 13.2 per cent.
2. Substance 5.0 grms. 25/500 = 1/20 taken  $\text{Fe}_2\text{O}_3$   
0.0331 = 13.2 per cent.

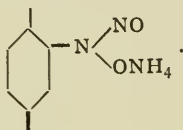
The analysis requires about one hour and a-quarter, but without inconvenience a number may be simultaneously carried out.

#### Preparation of Cupferron.

Sixty grms. of nitrobenzol, 1000 cc. of distilled water, and 30 grms. of  $\text{NH}_4\text{Cl}$  are thoroughly stirred up in a wide-mouthed bottle with an efficient stirring apparatus until a milky emulsion is formed. Into this emulsion (constant stirring) add 80 grms. of zinc dust (the amount depends on the quality) in very small portions at a time. During the addition of the Zn dust the temperature must be kept between 15° and 18° C. This may be accomplished by simply throwing pieces of ice into the rapidly whirling liquid from time to time. Continued vigorous stirring and the keeping of the temperature within the prescribed limits are the essentials which determine a good yield. The reduction is continued until the odour of nitrobenzol vanishes. The time required for the reduction

depends on the value of the zinc dust. It usually takes half-an-hour to reduce 60 grms. of nitrobenzol. The white zinc hydroxide is now filtered off with suction, and the filtrate cooled to  $0^{\circ}$  C. with ice, and ordinary salt (NaCl) is added to saturation. In a little while a thick mass of snow-white crystals fall. Filter off right away with suction, and dry the crystals between filter-paper. The yield of phenylhydroxylamine is usually about 70–85 per cent of the theory. As phenylhydroxylamine solutions are vigorous skin poisons and may pass through the unbroken skin into the blood, the hands should be washed with water and alcohol in case they come in contact with such solutions.

The freshly prepared phenylhydroxylamine is dried for an hour between filter-paper, and then dissolved in 300–500 cc. of commercial ether. The ether solution is filtered through a dry filter and cooled to  $0^{\circ}$  C. Into this cold solution dry ammonia gas is passed for about ten minutes, and then add somewhat more than the theoretical amount (more than 1 mol.) of fresh amyl nitrite all at once. The clear solution will suddenly get hot, and the entire vessel will be filled with snow-white crystals of the ammonium salt of nitrosophenylhydroxylamine—



The brilliant snow-white crystals are filtered off with suction, washed with ether, and dried between filter-paper. They are then to be placed in a well closed bottle with a small piece of solid ammonium carbonate.

The salt prepared and preserved in this manner will be found a welcome and thoroughly satisfactory precipitating and separating agent for copper and iron in any busy laboratory.—*Journal of Industrial and Engineering Chemistry*, iii., No. 9.

## THE DETECTION OF SALICYLIC ACID.

By H. C. SHERMAN and A. GROSS.

For the detection of salicylic acid, especially when present in small amounts, it is customary in many laboratories to rely upon the violet reaction with ferric chloride, almost to the exclusion of other tests. The popularity of the ferric chloride test is readily explained by its simplicity and delicacy. Using fresh 1 per cent ferric chloride as reagent the test is delicate in our hands to a dilution of about 1 : 400,000 when applied to 10 cc. of solution, about 1 : 750,000 to 1 : 1,000,000 if 25 cc. of solution be tested. The violet colour obtained with such small amounts of salicylic acid must be observed quickly as it fades rapidly, passing through a rose-red colour. A faint rose colour may also be obtained on addition of ferric chloride to solutions containing salicylic acid in amounts too small to show violet reaction.

Unfortunately, however, the formation of a violet colour with ferric chloride is a reaction by no means confined to salicylic acid. Mulliken's tables ("The Identification of Pure Organic Compounds") include many colourless compounds which give more or less distinctly violet reactions with ferric chloride, and some of these also resemble salicylic acid in solubilities. That this may lead to error in the testing of foods for salicylic acid has been pointed out by several writers (Brand, *Ztschr. f. de Ges. Brauw.*, xv., 303; *Ber.*, xxvii., 806; Erich, *Der Bierbrauer*, xxiv., 465; Munsche, *Woch. f. Brauerei*, x., 739; Abraham, *Journ. de Pharm. de Liège*, v., 173; Backe, *Annales des Falsifications*, Nov., 1909; Sherman, *Journ. Ind. and Eng. Chem.*, ii., 24; Backe, *Comptes Rendus*, cl., 540; *cli.*, 78).

Among the tests for salicylic acid, other than the ferric

chloride reaction, are the formation of the methyl ester or the nitro-compound, the reactions with bromine water and with Millon's reagent, and the Jorissen test.

The adoption by Mulliken of the methyl-ester and nitration tests for the identification of salicylic acid is sufficient evidence of their value for cases in which enough salicylic acid is involved to make them available; but these tests and also the test with bromine water seem not to be sufficiently delicate for the detection of very small amounts.

In tests with Millon's reagent it was found that heating for some time increases considerably the delicacy of the test. When two drops of Millon's reagent were added to the solution to be tested, shaken in a test-tube, and immersed in a boiling-water bath with a blank test for comparison, there was developed in the course of forty-five minutes' heating a delicate reddish or pink colour, even in the presence of only minute amounts of salicylic acid. With practice and with blank tests for comparison no difficulty was found in detecting the presence of 1 part salicylic acid in 2,000,000 of water when 20 cc. were tested; when only 10 cc. were tested, the pinkish tint was barely perceptible at this dilution. Longer heating and variations in the amount of reagent added were tried without appreciably altering the result. The limit of delicacy of the test with Millon's reagent as here used seems, therefore, to be reached by heating in boiling water for forty-five minutes and to lie at a dilution of about 1 : 2,000,000.

The Millon reaction also has the advantage over the ferric chloride test that the colour produced even with very small amounts of salicylic acid shows no evidence of fading on standing over night; but on account of the large number of substances which respond to the Millon reagent (Vaubel, *Zeit. Angew. Chem.*, 1900, p. 1125; Nasse, *Pflüger's Archiv*, 1901, lxxxiii., 361; Mann, "Physiological Histology," pp. 321–23; and "Chemistry of the Proteids," p. 7) it seems unlikely that this reaction will prove as useful as that of Jorissen.

The Jorissen reaction (*Bull. Acad. Roy. des Sciences, &c., Belgique*, 3rd series, iii., 259) has been used by a number of European investigators (da Silva, *Comptes Rendus*, cxxxi., 423; Klett, *Pharm. Centr.*, xli., 452; *Zeit. Unters. Nahr. Genussm.*, iv., 469; Portes and Desmoulières, *Ann. Chim. Anal.*, vi., 401; *Zeit. Unters. Nahr. Genussm.*, v., 468; Windisch, *Ibid.*, vi., 447) for the identification of small amounts of salicylic acid, and was found useful by one of us (Sherman, *Journ. Ind. and Eng. Chem.*, ii., 24) as a means of distinguishing between salicylic acid and maltol or isomaltol when present in small quantity in foods.

In further experiments with this reaction we have found that by diminishing the amount of copper used and increasing the time of heating, the test can be made much more delicate than appeared in our earlier work, in which the test was used in its original form, and considerably more delicate than the ferric chloride reaction. The longer heating is necessary to fully develop the characteristic colour, at least when only very small amounts of salicylic acid are present, and the reduction in the amount of copper diminishes the slight green colour due to the reagent which otherwise may interfere with the more delicate tests.

The test as now used for very small amounts of salicylic acid is as follows:—Bring the solution to be tested into a test-tube, add 4–5 drops of 10 per cent sodium or potassium nitrite, 4–5 drops of 50 per cent acetic acid, and 1 drop of 1 per cent copper sulphate. Shake after addition of each reagent, and finally place in a boiling-water bath in such position that the test liquid is completely immersed in the boiling water, and allow to stand for forty-five minutes, then remove, allow to cool, and examine against a white background, viewing the tube both vertically and horizontally, and comparing with a blank test in which the same amounts of reagents have been added to pure water.

In this way the presence of as little as 0.005 to 0.1 mgm. of salicylic acid in pure water solution can be



detected. Faint but perceptible reactions were obtained with 5 to 8 cc. of a solution of 1 : 1,000,000, and with 18 to 25 cc. of solution of 1 : 3,000,000 to 1 : 3,500,000.

No advantage has been found in a brine-bath over a water-bath, in longer heating than forty-five minutes, nor in varying the amounts of nitrite and acetic acid used. When larger amounts of salicylic acid are present a drop of stronger copper sulphate solution may be used, up to a 10 per cent solution as originally recommended. Except with very small amounts of salicylic acid the red colour of the Jorissen reaction develops quickly on heating, and the long immersion in the water-bath then becomes unnecessary if only qualitative results are required.

A feature which will be of great importance in colorimetric estimations of small amounts of salicylic acid is that, while the violet colour of the ferric chloride test fades rapidly, the red colour of the Jorissen test is quite stable. Even the faint colours obtained by long heating, where only very minute amounts of salicylic acid are involved, have shown no deterioration when allowed to stand over night.

It has also been found that the ferric chloride and Jorissen tests may be applied to the same solution of salicylic acid. After making the ferric chloride test the liquid may be diluted until the violet colour disappears and then submitted to the Jorissen reaction, when, if salicylic acid is present, pink colour will appear.

No extended study seems to have been made to determine what other substances will give red or pink reactions in the Jorissen test. Jorissen, in describing his reaction, stated that phenol behaves in the same way as salicylic acid, but benzoic acid does not. Allen states that neither benzoic, cinnamic, nor tartaric acid responds to the Jorissen test, which statement we have confirmed.

Special importance attaches to the behaviour in the Jorissen test of those substances which give violet reactions with ferric chloride. Maltol and isomaltol have already been considered; a few others have been tested, with the following results:—

Phenol, in our hands, gives the same colour as salicylic acid in both the Millon and the Jorissen tests, but the limits of delicacy are quite different. Phenol can be detected by the Millon reaction to about 1 : 2,000,000. In the Jorissen test phenol 1 : 100,000 gives practically the same colour as salicylic acid 1 : 1,000,000.

Saligenin gives, in the Jorissen reaction, a red colour at 1 : 10,000; a yellowish tint at 1 : 100,000; no reaction at 1 : 1,000,000. The limit of delicacy for the ferric chloride reaction with saligenin lies between 1 : 10,000 and 1 : 20,000.

2-Oxy-isophthalic acid gives the Jorissen reaction up to a dilution of 1 : 100,000, but is easily distinguished from salicylic acid in the colour which it gives with ferric chloride.

Methyl-ethyl-aceto-acetate, which gives, with ferric chloride, a violet-red colour in concentrated solutions, gives neither the Millon nor the Jorissen reaction when tested at a dilution of 1 : 1000.

Orchin, arbutin, resorcin, and phlorizin, which give blue, violet, or red-violet reactions with ferric chloride, do not respond to the Jorissen test.—*Journal of Industrial and Engineering Chemistry*, iii., No. 7.

**Molecular Refraction of Azotic Compounds.**—H. Duval.—The solvent appears to have an appreciable influence on the value of the molecular refraction. The position of the substituent in the ortho- or meta-positions gives such a slight variation in the molecular refraction that no conclusions can be drawn as to the difference in composition of the compounds. Rise of temperature causes a slight but steady increase in the value of the molecular refraction. The values calculated on the basis of Brühl's law of atomic additivity are decidedly lower than those obtained by experiment.—*Bull. Soc. Chim. de France*, xi—xii., No. 1.

## QUICK COMBINATION METHODS IN SMELTER ASSAYS.\*

By A. T. FRENCH.

(Continued from p. 91).

### INTERFERENCES AND SOURCES OF ERROR.

#### I. Mutual Interference of Lead and Lime.

LEAD and lime are both present as sulphates after taking down the assay to white fumes with sulphuric acid, and it is difficult, if not impossible, to effect a satisfactory separation by washing out the  $\text{CaSO}_4$ . This difficulty is avoided in the method suggested by doing the lead and the lime on separate portions; keeping back all the lead and a little lime in "A<sub>2</sub>," and dissolving all the lime and most of the lead in "A<sub>1</sub>."

This separation and the effect of the presence of lime in the lead titration, and of lead in the lime estimation, is shown in the following experiments:—

#### EXPERIMENT 1.—Separation of Lead or Lime—

0.05 gm. Pb } = 10 per cent lead, 10 per cent lime, 14 per  
0.05 " CaO } cent iron on  $\frac{1}{2}$  gm. assay.  
0.07 " Fe }

(a) The above quantities were dissolved, taken to fumes with  $\text{H}_2\text{SO}_4$ , diluted and cooled;  $\text{PbSO}_4$  was filtered off and estimated by the molybdate method, ferric hydrate precipitated twice with  $\text{NH}_4\text{HO}$ , CaO in the filtrate was thrown down as oxalate, and estimated volumetrically by permanganate method. Found—Pb, 9.9; CaO, 9.5.

Same, but with double quantity of Pb and CaO (= 1 gm. assay). Found—Pb, 9.9; CaO, 9.25.

(b) Same quantities, adding HCl after dilution, boiled, filtered, and washed with hot water.

Ferric hydrate precipitated once with  $\text{NH}_4\text{HO}$ . Found—CaO, 9.6, 9.7.

Ferric hydrate precipitated twice with  $\text{NH}_4\text{HO}$ . Found—CaO, 9.8, 9.9.

#### EXPERIMENT 2.—Interference of Lead with Lime Assay.

—The following mixtures were dissolved, taken to fumes with  $\text{H}_2\text{SO}_4$ , diluted HCl added, boiled, and washed with hot water. Ferric hydrate (when present) precipitated once with  $\text{NH}_4\text{HO}$ , CaO thrown down as oxalate, and estimated volumetrically by permanganate:—

0.05 CaO, 0.05 Fe, 0.05 Pb. CaO found, 9.8 ( $\frac{1}{2}$  gm. assay).

0.05 CaO, 0.05 Fe, 0.10 Pb. CaO found, 9.8.

0.05 CaO, 0.10 Pb. CaO found, 9.9.

Interference nil.

#### EXPERIMENT 3.—Interference of Lime with Lead Assay

by Molybdate.—The following mixtures were dissolved, taken to fumes with  $\text{H}_2\text{SO}_4$ , diluted, cooled, and washed with cold water:—

0.1 gm. Pb, 0.2 CaO, 0.05 Fe. Found—Pb, 9.8 (1 gm. assay).

Repeated—9.8, 9.9.

0.1 gm. Pb, 0.5 CaO, 0.1 Fe. Found—Pb, 9.9, 10.0.

0.1 gm. Pb, 0.1 gm. CaO, dissolved direct in acetic acid and ammonium acetate. Found—Pb, 10.2.

Repeated—10.4.

From this it will be seen that the amount of lime left with the lead sulphate in Method "A<sub>2</sub>" will not appreciably affect the assay.

#### II. Resolution of Ferric Hydrate Precipitate on Boiling of all $\text{NH}_4\text{HO}$ .

Re-precipitation of this dissolved iron as oxalate, giving low iron and high lime results. Similar effect with basic acetate separation. Retention of zinc by the hydrate precipitate in absence of excess of  $\text{NH}_4\text{HO}$ .

\* A Paper discussed at a Meeting of the Institution of Mining and Metallurgy, held at the Rooms of the Geological Society, Burlington House, Piccadilly, W., on Thursday, February 15th, 1912.

In Method "A<sub>2</sub>," the hydrates of iron and alumina are thrown down and filtered off; the filtrate thus obtained contains lime and zinc. The following experiments show why this solution cannot be utilised for their estimation:—

EXPERIMENT 4.—*Separation of Iron and Lime*.—The following quantities were weighed out, brought into solution as chlorides, with excess of HCl and NH<sub>4</sub>Cl present. 0.05 gm. CaO, 0.1 gm. Fe (equivalent to 10 per cent CaO and 20 per cent Fe on  $\frac{1}{2}$  gm. assay):—

- (a) Ferric hydrate precipitated once with NH<sub>4</sub>HO in excess. Found—CaO, 9.6, 9.7 (volumetric).
- (b) Ferric hydrate precipitated twice with NH<sub>4</sub>HO in excess. Found—CaO, 9.9, 9.8 (volumetric).
- (c) Ferric hydrate precipitated once with NH<sub>4</sub>HO, boiling off excess. Found—CaO, 10.4, 10.4, 10.6 (volumetric).
- (d) Ferric hydrate precipitated once with NH<sub>4</sub>HO, boiling off excess. Found—CaO, 10.6, 10.6 (gravimetric).  
FeO<sub>2</sub>O<sub>3</sub> found in CaO precipitate, 0.8, 0.6.
- (e) Ferric hydrate precipitated once with NH<sub>4</sub>HO, boiling off excess.
  1. Added NH<sub>4</sub>HO boiled and allowed to stand before adding the oxalate—no precipitate formed. Found—CaO, 10.4.
  2. Acidified the filtrate, added 2 cc. HNO<sub>3</sub>, boiled, then added excess of NH<sub>4</sub>HO—no precipitate formed. Found—CaO, 10.4.
  3. Passed H<sub>2</sub>S through the solution before adding the oxalate. The solution darkened, but no precipitate formed. Found—CaO, 10.5.
- (f) Iron precipitated once as basic acetate.  
Found—CaO, 10.6 volumetric  
10.4 gravimetric.  
Fe<sub>2</sub>O<sub>3</sub> found in CaO precipitate, 0.6.

EXPERIMENT 5.—*Separation of Zinc from Iron and Alumina*.—The following quantities were weighed out, brought into solution as chlorides with excess of HCl and NH<sub>4</sub>Cl present:—

0.1 gm. Zn, 0.1 gm. Fe, 0.05 Al<sub>2</sub>O<sub>3</sub> (equivalent to 20 per cent Zn, 20 per cent Fe, and 10 per cent Al<sub>2</sub>O<sub>3</sub> on  $\frac{1}{2}$  gm. assay).

- (a) Hydrates precipitated twice with NH<sub>4</sub>HO in excess.  
Zn found, 19.8, 20.0.
- (b) Hydrates precipitated once with NH<sub>4</sub>HO, boiling off excess. Zn found, 12.4, 12.8.
- (c) Same as (b) .. .. . Zn found 9.6  
Al<sub>2</sub>O<sub>3</sub> extracted from hydrates with caustic, filtered off ferric hydrate, solution acidified with HCl, Al<sub>2</sub>O<sub>3</sub> precipitated with slight excess of NH<sub>4</sub>HO, and filtered off.  
Zn found in filtrate 2.2  
Ferric hydrate precipitate re-dissolved and re-precipitated with excess of NH<sub>4</sub>HO, filtered .. .. . Zn found in filtrate 8.0  
Total 19.8
- (d) With smaller quantities.  
0.056 Zn, 0.07 Fe, 0.015 Al<sub>2</sub>O<sub>3</sub>  
(equivalent to 11.2 per cent Zn, 14 per cent Fe, and 3 per cent Al<sub>2</sub>O<sub>3</sub> on  $\frac{1}{2}$  gm. assay).  
Hydrates precipitated once with NH<sub>4</sub>HO, boiling off excess .. .. . Zn found 8.6  
Hydrates re-dissolved and re-precipitated with NH<sub>4</sub>HO in excess .. .. . Zn found in filtrate 2.6  
Total 11.2

### III. Interference of Manganese with the Estimation of Zinc (by Ferrocyanide) and Lime (by Permanganate).

EXPERIMENT 6.—*Manganese and Zinc*.—The following quantities were weighed out and brought into solution as chlorides with excess of HCl and NH<sub>4</sub>Cl present:—

- 0.07 gm. ZnO, 0.10 gm. Fe  
(equivalent to 14 per cent ZnO and 20 per cent Fe on  $\frac{1}{2}$  gm. assay).
- (a) Ferric hydrate precipitated twice with NH<sub>4</sub>HO, ZnO found .. .. . 14.0
  - (b) Same, adding 0.01 Mn (= 2 per cent on  $\frac{1}{2}$  gm. assay), ZnO found .. .. . 14.9
  - (c) Same, adding 0.02 Mn, ZnO found .. .. . 16.4
  - (b<sub>1</sub>) Same as b, but adding bromine water before precipitating hydrates, ZnO found .. .. . 14.0
  - (c<sub>1</sub>) Same as c, but adding bromine water before precipitating hydrates, ZnO found .. .. . 14.2
  - (d) Same as a, adding 0.06 Mn and bromine water before precipitating hydrates, ZnO found .. 19.5
  - (d<sub>1</sub>) Same as d, acidifying filtrate from hydrates, adding more bromine and rendering alkaline with NH<sub>4</sub>HO. More Mn separated on standing; the filtrate from this gave ZnO .. 14.2  
Repeated 14.2

The above shows the necessity of removing manganese before proceeding with the zinc estimation.

Small quantities, up to about one-fourth of the iron present, can be thrown down with the hydrates by adding bromine water before adding NH<sub>4</sub>HO to the solution. When a larger proportion is present, shown by the hydrate precipitate being very dark, almost black in colour, it is necessary to test the acidified filtrate again with bromine water; if, on further adding a slight excess of NH<sub>4</sub>HO and warming, more manganese separates out, this must be filtered off before proceeding with the assay.

EXPERIMENT 7.—*Manganese and Lime*.—0.05 gm. CaO and 0.1 gm. MnSO<sub>4</sub> were weighed out, dissolved in HCl, excess of NH<sub>4</sub>HO and ammonium oxalate added, the precipitate filtered off, washed, dissolved in dilute H<sub>2</sub>SO<sub>4</sub>, and titrated with permanganate.

Found—CaO, 0.05 gm. (= 10 per cent on  $\frac{1}{2}$  gm. assay).

Repeated .. .. . 10 per cent

Manganese does not appear to interfere with the estimation of lime by permanganate.

### IV. Interference of Oxalic Acid with the Estimation of Zinc (by Ferrocyanide).

If the solution from which lime has been precipitated by adding an excess of ammonium oxalate is used for the estimation of zinc, oxalic acid will be present after acidulating the solution with HCl in the ordinary way. Oxalic acid interferes with the titration of zinc by ferrocyanide if this is carried out, as usually recommended, with the solution nearly boiling, causing the colour of the end reaction to fade and bringing results high. The author finds, however, that the titration can be carried out quite well at about 30° C. or even at room temperature (about 15° C.), and that at these temperatures oxalic acid has no effect on the titration.

EXPERIMENT 8.—*Oxalic Acid and Zinc*.—

(a) Three solutions containing 0.1 gm. zinc were acidulated with HCl, adding 5 cc. in excess, gassed, and H<sub>2</sub>S boiled off. They were titrated (with ferrocyanide):—

Boiling .. .. . 10.3 cc.  
Warm (about 30° C.) .. .. . 10.2 "  
Cold .. .. . 10.1 "

(b) To similar solutions, 20 cc. of a solution of (2 per cent) ammonium oxalate were added before acidulating with HCl.

Boiling .. .. . 10.4 cc.  
Warm .. .. . 10.3 "  
Cold .. .. . 10.3 "

(c) Same as (b), but adding 50 cc. ammonium oxalate.

Boiling .. .. . 10.6 cc.  
Warm .. .. . 10.4 "  
Cold .. .. . 10.3 "

(End reaction faded).



THE SEPARATE DETERMINATIONS.

*Alumina.*

1. *Phosphate Method.*—To a cold neutral oxidised solution of the bases, freed from large quantities of As, Sb, and Cu, 2 to 3 cc. of HCl, solutions containing 2 grms. of sodium phosphate, and 10 grms. of sodium hyposulphate are added, then 15 cc. of acetic acid (glacial acid one part, water one part). The solution is made up to about 300 cc., boiled vigorously for twenty minutes, filtered, washed with hot water, ignited in the front of the muffle, and weighed as  $\text{Al}_2\text{PO}_4$ .  $\text{Al}_2\text{O}_3 = \text{Al}_2\text{PO}_4 \times 0.4185$ .

2. *Extraction by Caustic.*—To an acid solution of the bases a slight excess of  $\text{NH}_4\text{HO}$  is added, and the solution boiled until it no longer smells of ammonia; the precipitated hydrates are filtered off, washed, and then washed back into a glazed porcelain dish; 1 to 2 in. of pure stick caustic soda or potash are added, and the dish placed in a warm place for a quarter of an hour. The solution is then filtered through the same paper.  $\text{Al}_2\text{O}_3$  passes through into the filtrate. The filtrate is acidified with HCl, a slight excess of  $\text{NH}_4\text{HO}$  added, the solution boiled until it no more smells of ammonia, and the precipitate filtered off, washed well, dried, ignited, and weighed as  $\text{Al}_2\text{O}_3$ .

The author finds that with small quantities of alumina and large amounts of zinc, lime, sulphates, &c., in the solution the phosphate method is apt to give erratic results. Under these conditions it is safer to throw down the hydrates, re-dissolve in 2 to 3 cc. HCl, and then add the phosphate, &c.

The extraction method is more tedious, but gives good results on small quantities of  $\text{Al}_2\text{O}_3$ . If more than 0.05 gm. of  $\text{Al}_2\text{O}_3$  is present (10 per cent in  $\frac{1}{2}$  gm. assay) the aluminium hydrate should be re-dissolved and re-precipitated or the two methods may be combined, extracting with caustic, acidulating the filtrate with HCl, adding 2 cc. in excess, and then the phosphate, &c.

*Interferences (Phosphate Method).*—Copper in large quantity is thrown down by the hyposulphite, and brings the results high. Smaller quantities (as in slags) do not interfere, probably being kept in solution as acetate. When thrown down, Cu colours the  $\text{Al}_2\text{PO}_4$  blue or black, according to their relative quantity.

Lead and manganese in ordinary quantity do not interfere.

Arsenic and antimony when in considerable quantity are thrown down and colour the precipitate, which, however, burns white. Results come a little high.

EXPERIMENT 9.—A solution was made up containing 0.031 gm.  $\text{Al}_2\text{O}_3$  and 0.1 gm. Fe (ferric) in 20 cc.

| To 20 cc. was added— | $\text{Al}_2\text{O}_3$ found— |
|----------------------|--------------------------------|
| 0.01 Cu              | 0.033 (bluish)                 |
| 0.01 "               | 0.031 (white)                  |
| 0.05 "               | 0.059 (black)                  |
| 0.05 Pb              | 0.032 (white)                  |
| 0.10 "               | 0.032 "                        |
| 0.03 Mn              | 0.031 "                        |
| 0.06 "               | 0.030 <sup>a</sup> "           |
| 0.04 Sb              |                                |
| 0.01 As              | 0.037 "                        |
| 0.02 Sb              |                                |
| 0.005 As             | 0.034 "                        |

Thus the impurities carried down in the hydrate precipitate in ores or those present ordinarily in slags do not interfere with the phosphate method.

*Copper.*

*Permanganate Method.*— $\text{KMnO}_4$ , 5.7 grms. per litre, 50 cc. = 0.1 Cu. The copper is brought into a solution containing 2 or 3 cc. free hydrochloric acid. If in nitric solution, it must be taken to dryness, and taken up with HCl. If in sulphuric, the solution is neutralised with  $\text{NH}_4\text{HO}$  and 2 or 3 cc. HCl added. If much insoluble is present this is filtered off; a little iron (about 0.05 gm.) should be added if none is present, as in treating a sulphide precipitate or in standardising.

The bulk of the solution should be 150 to 200 cc. To this is added 20 cc. of a 10 per cent solution of sodium sulphite (it is convenient to filter the solution into a beaker containing the sulphite), and then 5 cc. of a 10 per cent solution of ammonium sulphocyanide. The beaker is placed on the hot plate and brought to a boil, by which time the solution should be decolorised, otherwise more sulphite is added. After boiling a few minutes the solution is filtered through a double close-grained filter-paper and washed three times with hot water. The funnel is then placed over a flask and washed with a hot 8 per cent solution of caustic soda or potash. The beaker in which the precipitation was performed is also washed with caustic, and the washings poured through the funnel. The precipitate in the funnel is now washed three times with hot water, filtrate and washings made up to about 300 cc. with cold water, acidified with dilute  $\text{H}_2\text{SO}_4$ , adding at least 10 cc. in excess, and titrated cold with standard permanganate.

The same permanganate solution is used as for iron, the copper value of the solution being five times the iron value, but it is well to standardise on electrolytic copper.

The author finds the permanganate about the best all-round method for copper, being nearly as rapid as the cyanide (more so if the copper is precipitated with  $\text{H}_2\text{S}$  and As and Sb extracted), and having as good an end reaction as the thiosulphate.

Water, acid, and caustic solution used should be tested for anything which would affect permanganate. The advantage of adding iron to the checks and sulphide precipitates is shown by the following:—

EXPERIMENT 10.—(0.2 gm. Fe required 19.9 cc. permanganate).

0.1 gm. Cu required 49.5 cc. : 0.1 gm. Cu + 0.1 gm.  $\text{FeS}_2$  required 50.3.

0.05 gm. Cu required 24.6 cc. : 0.05 gm. Cu + 0.1 gm.  $\text{FeS}_2$  required 25.0.

0.025 gm. Cu required 12.0 cc. : 0.025 gm. Cu + 0.1 gm.  $\text{FeS}_2$  required 12.5.

The iron is conveniently added as  $\text{FeS}_2$  when the copper or sulphide precipitate is being dissolved in  $\text{HNO}_3$ , but iron wire or any pure iron salt will do equally well.

(To be continued).

## PROCEEDINGS OF SOCIETIES.

### PHYSICAL SOCIETY.

Annual General Meeting, February 9th, 1912.

Prof. H. L. CALLENDAR, F.R.S., President, in the Chair.

THE Report of the Council, read by the Secretary, and the Report of the Treasurer were adopted by the meeting.

A vote of thanks to the Auditors, moved by Dr. A. RUSSELL and seconded by Mr. D. OWEN, was carried unanimously.

A vote of thanks to the Council for the way in which they have served the Society, proposed by Mr. C. W. S. CRAWLEY and seconded by Mr. W. B. CROFT, was carried unanimously.

A vote of thanks to the Governors of the Imperial College for the use of their premises for the meetings of the Society, proposed by Dr. W. E. SUMPNER and seconded by Dr. W. H. ECCLES, was also carried unanimously.

The Council proposed Prof. H. Nagaoka for election as an Honorary Fellow, and submitted his name to the meeting, which unanimously endorsed the Council's selection.

The officers elected for the ensuing year were as follows:—

*President*—Prof. A. Schuster, Ph.D., F.R.S.

*Vice-Presidents*—Those who have filled the office of President, together with A. Campbell, B.A.; Prof. C. H. Lees, D.Sc., F.R.S.; Prof. T. Mather, F.R.S.; A. Russell, M.A., D.Sc.

*Secretaries*—W. R. Cooper, M.A., 82, Victoria Street, S.W.; S. W. J. Smith, M.A., D.Sc., Imperial College of Science and Technology, South Kensington.

*Foreign Secretary*—Prof. S. P. Thompson, D.Sc., F.R.S.

*Treasurer*—W. Duddell, F.R.S., 56, Victoria Street, S.W.

*Librarian*—S. W. J. Smith, M.A., D.Sc.

*Other Members of Council*—Prof. C. G. Barkla, D.Sc.; Prof. P. V. Bevan, M.A.; Major W. A. J. O'Meara, C.M.G.; S. Skinner, M.A.; F. E. Smith; Prof. the Hon. R. J. Strutt, F.R.S.; W. E. Sumner, D.Sc.; F. Twyman; R. S. Whipple; R. S. Willows, M.A., D.Sc.

Prof. A. SCHUSTER, Ph.D., D.Sc., LL.D., F.R.S., then took the Chair and delivered the Presidential Address on "*A Critical Examination of the Possible Causes of Terrestrial Magnetism.*"

In forming any theory of the cause of terrestrial magnetism, the first question that arises is whether we are to consider the near coincidence of the geographical with the magnetic axis as accidental or significant. The secular variation argues for the second alternative, and scientific opinion has always favoured the view that there is a definite reason for the close approach of the magnetic to the geographical pole.

The view that iron is responsible for the observed magnetic field has generally been put aside, because iron loses its magnetisation at temperatures lower than those which all are agreed must hold at moderate depths below the surface. But the objection raised on this ground disregards the possibility that the critical temperature of iron may be raised by pressure. It may be shown that if that temperature depends on molecular distance, and the ratio of compressibility to thermal dilatation is assumed to be independent of pressure, the rate of increase of temperature with the depth is less than the rate of increase of the critical temperature, so that iron would retain its magnetic properties. Experiments on the effects of pressure on the critical temperature of iron have been in progress during the last four years, but have not hitherto led to a decisive result. For the present we must, therefore, keep our minds open to the possibility that the iron contained in the earth is magnetisable.

The alternative opinion that electric currents circulating inside the earth are the cause of electric currents is next examined. Though this view seems to be favoured by scientific opinion, it has to overcome formidable difficulties before it can be accepted. Are the electric currents permanent, or are they only survivals of a former state of things which is dying out? If permanent, we must account for the electromotive forces, and we know of no such forces which could act in the manner required. If the electric currents are survivals, their intensity when the earth crust first formed must have been at least  $10^{12}$  times as strong as it is now, and the difficulty of accounting for their original production would be correspondingly increased. In the opinion of the author, the difficulties which stand in the way of basing terrestrial magnetism on electric currents inside the earth are insurmountable.

The question whether the rotation of the earth may be responsible for its magnetic field is next examined, and different possibilities are considered. If the rotation of a sphere independently of the chemical nature of the substance were to produce a magnetic field, it is shown by the theory of dimensions that the field at the surface of the sphere would be proportional to the angular velocity and independent of its size. The effect of rotating bodies set into rotation in our laboratories would give, therefore, magnetic forces equal to those of the earth with one rotation per day, and with angular velocities of the order of one

per second the effects would be so large that they could not have escaped detection.

A second supposition, that a neutral molecule in its motion behaves as if it carried a charge, leads to the result that if terrestrial magnetism be due to such a cause, the effects to be expected in any laboratory experiment that we could propose are far too small to be detected. But the theory is finally negated by the additional conditions which must be imposed to destroy the effects of translation independently of rotation. A distinction must here be made between possible magnetic effects of a rotatory body on a magnet which is at rest and on one the supports of which are fixed to the rotating body. Returning to the effects of rotation, the possibility is considered that rotation instead of directly determining magnetic intensity, determines magnetic force which may or may not cause magnetisation according to the nature of the body. This view deserves attention, because there is some theoretical foundation for it, inasmuch as molecules may be considered to behave in a manner analogous to that of a gyrostatic compass. The theory would also explain in a natural manner the secular variation by a precessional motion of a magnetic molecule. On the other hand, the theory would have to explain why the iron inside the earth becomes—by rotation—more strongly magnetised than the iron in our laboratories. There is, of course, always the possibility of some substance being subject to the effects of rotation in a much higher degree than iron. Such questions can only be settled by experiments which are now in progress. Other theories of the secular variation are considered.

In conclusion, the question is raised whether the negative electron is subject to gravitation, and if so, whether in comparing the weight of a negative electron with that of the unit positive charge, we must consider the proportionality between gravitation and mass to hold. In Lorentz's theory of gravitation this is abandoned. It is pointed out how fundamental questions have a bearing on the problem of terrestrial magnetism.

A vote of thanks to Prof. Schuster for his Presidential Address, moved by Prof. CALLENDAR and seconded by Dr. W. N. SHAW, was carried unanimously.

## INSTITUTE OF CHEMISTRY.

### "Cellulose."

MR. CHARLES F. CROSS, B.S., F.I.C., delivered his second lecture on "*Cellulose*" before the Institute of Chemistry, at University College, London, on Friday, February 23rd; Prof. J. Norman Collie, LL.D., F.R.S., presiding.

The celluloses as structural colloids are the end terms of a series of carbohydrates, exhibiting analogous properties in varying degrees, and the lecturer selected for demonstration of the series types of colloids of industrial importance.

*Starch*, and its derivative "*feculose*," extensively used in the production of surfaced "*Art*" papers; "*tragasol*," obtained from the endosperm of leguminous seeds, and also extensively used as a "gum" in textile finishes, leather dressing, &c.; "*cutiloid*," a new colloid obtained by chemical reaction from tragasol, and used as a tanning agent and in paper sizing; "*Japanese isinglass*," obtained from certain *Alga*, and exported from Japan to the extent of £200,000 per annum for consumption, chiefly in China, as a food stuff. These were compared with cellulose, hydrated and dissolved to structureless solutions and re-verting to hydrated massive forms or films.

The papermakers beating process was considered as a mechanical method of producing hydration effects, and the principle of the new "*Jackson*" beater was expounded, with specimens of its effects.

Questions of minute structure and dimensions, being inseparable from cellulose, the importance of comple



mentary histological observations and research is to be impressed upon young students. It was shown that typical reactions of cellulose can be studied in terms of surface dimensions of the reacting cellulose, also that approximate calculations can be made of surface dimensions of solids of natural, and therefore irregular or variable, minute structure, e.g., cotton.

In conclusion, the question of the world's supply of cellulose, past, present, and future was considered, and it was also pointed out that in the cellulose industries, mechanical and chemical, we are guilty of waste or destruction of substance, and therefore of value, on a colossal scale, much larger than the historical instances of the wastes of glycerin and coal distillation products, happily long since terminated.

Apart from the waste of wood, and wood by-products, attention was specially drawn to megasse, or sugar-cane refuse, and cotton-seed hull fibre, and the positive prospects of their utilisation.

The lecture was illustrated by specimens of feculose art paper, tragasol products, films, applications to textiles, cutiloid leather, Japanese isinglass in various forms, cellulose products—showing full range of hydration effects, and reversion, in the sphere of artificial silk, films, papers, and massive solids—papers and boards from megasse and cotton hull fibre.

## NOTICES OF BOOKS.

*A Text-book of Physics. Heat.* By J. H. POYNTING, Sc.D., F.R.S., and Sir J. J. THOMSON, M.A., F.R.S. Fourth Edition. London: Charles Griffin and Co., Ltd. 1911. (15s.).

THIS work occupies a unique position among text-books of physics, and for students whose knowledge of mathematics is limited to the elements of algebra, geometry, and the calculi it is unsurpassed. The third volume, which deals with heat, has reached its fourth edition, in which certain corrections have been made, as well as some additions and alterations. The descriptions of experiments are fully illustrated by diagrams, and the methods of calculating results from observations are explained by the working out of formulæ, only the most elementary mathematics being employed. The general accounts of radiation and of the second law of thermodynamics, both of which subjects frequently present great difficulty to the beginner, are excellently clear, and in every respect the book can be thoroughly recommended as a text-book of physics suitable for the use of first-year college students.

*The Colloidal and Crystalloidal State of Matter.* By Dr. PAUL ROHLAND. Translated by W. J. BRITLAND and H. E. POTTS, M.Sc. London: Constable and Co., Ltd. 1911. (4s. net).

To the general reader of culture and education this little book will make a special appeal. From the stores of his knowledge of technical chemistry the author has brought together such facts as seem to him to be of the widest general interest, and his skill in selecting his material is equalled only by his ability to state the gist of an important and far-reaching question in a very few words. He gives a clear and interesting account of the history of the growth of our knowledge of the chemistry of the colloidal state, pointing out the chief differences between crystalloids and colloids, and then proceeds to discuss the applications of colloidal chemistry to various branches of technics, such as cement making, soap making, &c. He makes some allusion to those aspects of the subject which are of particular interest to metaphysicians, and altogether gives

a stimulating and exceedingly interesting account of the chemistry of the colloidal state.

*Chemistry for Engineers and Manufacturers.* By BERTRAM BLOUNT, F.I.C., and A. G. BLOXAM, F.I.C. Vol. I., Second Edition. London: Charles Griffin and Co., Ltd. 1911. (14s.).

THE first volume of this short text-book of chemistry for engineers deals with subjects which are of special interest to mechanical engineers, builders, metallurgists, and those who are concerned with the construction of plant and the production of power. The range of subjects is wide, and the authors have not allowed themselves more space than suffices to give a brief outline of the most important and typical processes. The second edition has been thoroughly revised and brought up to date, and the most recent information is incorporated in the text.

*Transactions of the American Institute of Chemical Engineers.* Volume III. London: E. and F. N. Spon, Ltd. New York: Spon and Chamberlain. 1910. (25s. net).

THE *Transactions of the American Institute of Chemical Engineers* show that this young society is full of vigour, and is likely to rank in the future with the most important of similar associations. The third volume of transactions contains account of the meetings and excursions of the Society, as well as reprints of Addresses and papers read before it. The reports of the Committee on Education include interesting articles on the ideal training of the chemical engineer, with many expressions of opinion from eminent men as to the best means to adopt in order to ensure that the young chemist shall be given the most satisfactory education. Other articles include papers on plant design, sewage disposal, &c., while in one important paper the inventor, Dr. F. G. Wiechmann, gives a full account of a new product for use in the arts, to which he has given the name Protal. This substance, which is intended to take the place of rubber, seems likely to find many useful applications in the future.

## CORRESPONDENCE.

### ACTION OF OZONE ON CELLULOSE.

*To the Editor of the Chemical News.*

SIR,—I was unfortunately unable to be present at the meeting of the Chemical Society when Dr. Doree read his paper on "The Action of Ozone on Cellulose." From the account given me, it appears that the paper dealt principally with the academical or strictly scientific aspect of the case without going into the purely technical applications or results.

There is no doubt, however, that some misconception may arise as to the action or value of the use of ozone in bleaching operations generally. From the results which Dr. Doree showed, it is possible that the conception may arise that ozone is useless from the fact that it will destroy or rot any fibrous material. So far from this being the case I am able to state definitely that ozone, in proper strength or concentration for bleaching purposes, is perfectly harmless, and, so far as I have been able to test, it does not affect fibrous material to any extent which can be measured. As a means of measuring comparisons have been made between fibres which have been bleached in the ordinary method and those which have been bleached either by ozone alone or in combination, and it has been

proved that those fibres bleached by the ordinary methods were far less strong than those bleached by ozone, either alone or in combination. Naturally the strength or concentration of the ozone was many times weaker than that used by Dr. Doree.—I am, &c.

EDWARD L. JOSEPH,  
Managing Director, Ozonair, Limited.

96, Victoria Street, S.W.,  
February 19, 1912.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Note.*—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. cliv., No. 2, January 8, 1912.

**Catalytic Decomposition of Formic Ethers.**—Paul Sabatier and A. Mailhe.—In the absence of catalysers the formic ethers of primary alcohols are fairly stable, but they are very rapidly decomposed in the presence of various catalysers. Thus, with titanic oxide at 250° the reaction,  $\text{HCO}_2\text{C}_n\text{H}_{2n+1} = \text{CO} + \text{C}_n\text{H}_{2n+1}\text{OH}$ , occurs, and the same result is obtained with zinc oxide. With thorium oxide the predominant reaction is the above, but carbon dioxide and ether oxide are also formed:  $2(\text{HCO}_2\text{C}_n\text{H}_{2n+1}) = \text{HCOH} + \text{CO}_2 + (\text{C}_n\text{H}_{2n+1})_2\text{O}$ . With divided metals (platinum, nickel, &c.) formic acid is rapidly decomposed into  $\text{CO}_2$  and hydrogen, and formic ethers undergo the decomposition expressed by the first of the above equations.

**Action of Nitrogen and Oxygen on Magnesium.**—C. Matignon and M. Lassieur.—Nitrogen combines directly with magnesium above 670°. Oxygen begins to act on it at 600°. Between 670° and 600° the nitrogen can be isolated from a mixture of oxygen and nitrogen; above 670° magnesium fixes the two elements at very unequal rates. The addition of mercury does not facilitate the combination of nitrogen and oxygen.

**Action of Amino-acids on Sugars.**—L. C. Maillard.—When sugars are treated with amino-acids carbon dioxide is generated, and melanoidines of unknown composition separate in the form of blackish deposits. The reaction is general, and takes place extremely easily.

*Bulletin de la Société Chimique de France.*  
Vol. xi.—xii., No. 1.

**Action of Heat on Ochres.**—A. Bouchonnet.—When certain ochres are heated to the melting-point of silver they are converted into a different modification which the author calls the  $\alpha$ -variety. Apparently in this form the  $\text{Fe}_2\text{O}_3$  is partially converted into  $\text{Fe}_3\text{O}_4$ , and this conclusion is confirmed by the fact that the  $\alpha$ -variety is magnetic. The magnetism disappears after prolonged heating, but reappears at 1600°.

**Use of Fluoresceine to Detect Bromine.**—H. Baubigny.—The author brings forward further evidence to prove that fluoresceine is a convenient and sensitive reagent for bromine, which Pribram has called in question. He regards fluoresceine paper, freshly prepared, as an irreproachable means of detecting traces of bromine.

**Decomposition of Aldazines by Heat.**—Paul Pascal and Léon Normand.—Aromatic azines decompose at about 300°, losing nitrogen and ammonia, and yielding a stilbene derivative. The yield is increased when the hydrogen in

the aromatic group, which is in the ortho-position as regards the  $-\text{CH}=\text{N}_2=$  group is replaced by any group whatever. The yield of stilbene derivative is decreased as the molecular weight of the azine increases. When one of the groups substituted in the azine nuclei possesses a residual affinity, like the groups  $\text{OH}$  or  $\text{ArH}_2$ , the yield of stilbene derivative is lowered. When several phenol functions are attached to each aromatic nucleus of the azine it is difficult to get good yields of the corresponding stilbene compounds.

**Methoxy-benzoylacetic Ethers.**—A. Wahl and C. Silberzweig.—The authors have prepared the methoxy-benzoylacetic ethers of ethyl and methyl, by the condensation of the ethyl or methyl acetic ether with methoxybenzoic ethers in presence of sodium. The action of mineral acids on the copper salt of metamethoxybenzoylacetic ether gives the  $\delta$ -ketonic ether.

## MEETINGS FOR THE WEEK.

MONDAY, 4th.—Royal Society of Arts, 8. (Cantor Lecture). "The Loom and Spindle—Past, Present, and Future," by Luther Hooper.

Royal Institution, 5. General Monthly Meeting.

Society of Chemical Industry, 8. "The Photographic Process," by C. E. K. Mees. "Estimation of Glucose in Leather," by J. Gordon Parker and J. R. Blockey.

TUESDAY, 5th.—Royal Institution, 3. "Optical Determination of Stress, and some Applications to Engineering Problems," by Prof. E. G. Coker, F.R.S.E., &c.

WEDNESDAY, 6th.—Royal Society of Arts, 8. "Some Modern Problems of Illumination—the Measurement and Comparison of Light Sources," by T. Thorne Baker. Society of Public Analysts, 8. "Method of Estimating Calcium Carbonate in Soils," by H. S. Shrewsbury. "Standards for Malt Vinegar," by A. C. Chapman. "Estimation of Ammonia in Carbonated Waters," by G. D. Elsdon and N. Evers. "New Preservative for Milk, Cream, &c.," by G. A. Stokes.

THURSDAY, 7th.—Royal Institution, 3. "Wellington's Army," by Prof. Charles Oman, M.A., &c.

Royal Society. "Devitrification of Silica Glass" and "Volatility of Metals of the Platinum Group," by Sir William Crookes. "An Optical Load-extension Indicator, together with some Diagrams obtained therewith," by W. E. Dalby. "Velocity of the Secondary Cathode Particles ejected by the Characteristic Röntgen Rays" and "Transmission of Cathode Rays through Matter," by R. Whiddington. "Voltage Effect in Selenium," by E. E. Fournier d'Albe.

Chemical, 8.30. "Isomeric Change of Diacyl anilides into Acylaminoketones—Transformation of Dibenzoylparachloro- (and Parabromo-) aniline into the Isomeric Benzoylchloro- (and Bromo-) amino Benzophenone," by A. Angel. "Chemistry of the Glutaconic Acids—Part III., Glutaconic Acid and its  $\beta$ -Alkyl Derivatives," by N. Bland and J. F. Thorpe. "Asymmetric Quinquevalent Nitrogen Compounds of Simple Molecular Constitution," by W. J. Pope and J. Read. "Interaction of Phosphorus and Potassium Hydroxide Solution," by M. N. Banerjee. "The Triazogroup—Part XX., Azolimides of the Propane Series," by M. O. Forster and J. C. Withers. "Synthesis of Glyoxaline Derivatives allied to Pilocarpine," by F. L. Pyman. "Calcium Nitrate—Part I., The Three-component System—Calcium Nitrate, Nitric Acid, Water—at 25°," by H. S. Taylor. "Calcium Nitrate—Part II., The Two-component System—Calcium Nitrate, Water," by H. Bassett, jun., and H. S. Taylor. "Viscosity and Association—Part II., Viscosity of Geometrical Isomerides," by F. B. Thole. "Chemistry of the Glutaconic Acids" (a Correction), by J. F. Thorpe. "Azo-salicylic Acid and Azo-oxy-naphthoic Acid Dyes," by A. C. Sircar and E. R. Watson. "Catalytic Action of Copper at 300° C., on some Alcohols of the Terpene Group," by G. B. Neave.

FRIDAY, 8th.—Royal Institution, 9. "The Effects of the Thirty Years' War," by Dr. A. W. Ward.

SATURDAY, 9th.—Royal Institution, 3. "Molecular Physics," by Sir J. J. Thomson, F.R.S., &c.



# THE CHEMICAL NEWS.

VOL. CV., No. 2728.

## A NEW METHOD FOR THE SEPARATION OF THORIUM.

By T. O. SMITH and C. JAMES.

WHILE working upon the separation of thorium from the rare earths the authors observed that sebacic acid gave a precipitate in a neutral solution which appeared to be quantitative.

Thorium sebacate is a voluminous granular precipitate which settles readily and is easily filtered. Solutions of cerium, lanthanum, yttrium, &c., give no precipitate with sebacic acid even upon boiling.

In order to determine whether or not the above observations were correct, the following work was carried out.

A thorium nitrate solution was prepared, carefully standardised by the oxalic acid and hydrogen peroxide methods, and was found to contain 0.005572 grm. of thorium dioxide per cubic centimetre.

The precipitant was used in the form of a boiling solution practically saturated at that temperature.

Fifty cc. portions of the standard thorium nitrate solution were measured into a 250 cc. beaker and raised to the boiling-point. A slight excess of the hot solution of sebacic acid was added slowly, with continuous stirring. The precipitate, which formed at once, was immediately filtered and thoroughly washed with boiling water. The sebacate washes readily, and the operation may be performed with ease in a very short time. The precipitate was rapidly dried, ignited, and weighed as thorium dioxide.

The following data shows a good agreement with the standardisation by oxalic acid:—

| No. of cc. of standard thorium solution. | Grms. ThO <sub>2</sub> precipitated by oxalic acid. | Grms. ThO <sub>2</sub> precipitated by sebacic acid. |
|------------------------------------------|-----------------------------------------------------|------------------------------------------------------|
| 50                                       | 0.2791                                              | 0.2787                                               |
| 50                                       | 0.2786                                              | 0.2785                                               |
| 50                                       | 0.2780                                              | 0.2786                                               |
| 50                                       | 0.2783                                              | 0.2790                                               |
| 50                                       | 0.2787                                              | 0.2792                                               |
| 50                                       | 0.2790                                              | 0.2790                                               |
| Average ..                               | 0.2786                                              | 0.2788                                               |

The next step was to ascertain the effect of the presence of rare earths upon the thorium precipitate. Accordingly a solution consisting chiefly of cerium, together with fair amounts of lanthanum, praseodymium, neodymium, and traces of samarium, gadolinium, &c., was prepared. Varying quantities of this solution, which contained 0.005516 grm. of the combined oxides per cc., were added to the standard thorium solution. The thorium dioxide was determined as above.

Results are given below:—

| No. of cc. of standard thorium solution. | Grms. of rare earth oxides present. | ThO <sub>2</sub> present by average of oxalic and sebacic standardisation. | ThO <sub>2</sub> found. |
|------------------------------------------|-------------------------------------|----------------------------------------------------------------------------|-------------------------|
| 50                                       | 0.05516                             | 0.2787                                                                     | 0.2789                  |
| 50                                       | 0.11032                             | 0.2787                                                                     | 0.2786                  |
| 50                                       | 0.16548                             | 0.2787                                                                     | 0.2789                  |
| 10                                       | 0.5516                              | 0.5574                                                                     | 0.0562                  |
| 10                                       | 0.5516                              | 0.5574                                                                     | 0.0565                  |
| 10                                       | 0.5516                              | 0.5574                                                                     | 0.0564                  |

The authors did not test the action of salts such as dysprosium, erbium, thulium, &c., upon the thorium precipitate, as these elements occur only in small amounts in the ordinary thorium minerals.

## Separation of Thorium from the Rare Earths.

The reaction between sebacic acid and neutral thorium solutions would appear to be valuable for the separation and purification of thorium materials.

Sebacic acid can probably be prepared more cheaply than the reagents ordinarily used for the more rapid purification of thorium. It is formed when castor-oil soap is heated with sodium hydroxide. It dissolves in 1000 parts of water at 17°, 40 parts per litre at 65°, and at the boiling-point becomes fairly soluble. Owing to its slight solubility in cold water it can readily be recovered; hence it could be used in the separation of thorium on a large scale.

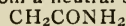
### Qualitative Tests with other Acids.

Phenoxyacetic acid, CH<sub>2</sub>(OC<sub>6</sub>H<sub>5</sub>)COOH, precipitated thorium from a neutral solution almost quantitatively. The addition of aniline did not aid in the separation. It was therefore considered that thorium phenoxyacetate was very slightly soluble in water.

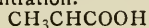
The ortho-nitro-phenoxyacetic acid did not give satisfactory results.

Mucic acid, (CHOH)<sub>4</sub>(COOH)<sub>2</sub>, gave a precipitate which filtered slowly and was not quantitative.

Anisic acid, C<sub>6</sub>H<sub>4</sub>(OCH<sub>3</sub>)COOH, only partially precipitated thorium from a neutral solution.



Aspartic acid,  $\begin{array}{c} | \\ \text{CH}_2\text{COOH} \end{array}$ , when boiled with a neutral solution of thorium nitrate gave a precipitate which could not be separated by filtration.



Pyrotartaric acid,  $\begin{array}{c} | \\ \text{CH}_2\text{COOH} \end{array}$ . The addition of this acid to a cold neutral solution of thorium nitrate caused no precipitation. However, upon boiling a curdy precipitate rapidly formed, and after filtering no thorium was found in the solution. From the above facts it would seem that pyrotartaric acid could be used for the quantitative determination of thorium.

Since the cost of pyrotartaric acid is considerably greater than sebacic acid, and since the former cannot be regained so readily, no further work was done with it.

Oxanilic acid, C<sub>6</sub>H<sub>5</sub>NHCOCOOH, precipitates both the rare earths and thorium from neutral solutions. From slightly acid solutions thorium only is precipitated. By increasing the concentration of the acid the precipitate re-dissolves.

All the above acids, with the exception of oxanilic, give no precipitate with the rare earths in cold or hot neutral solutions.

New Hampshire College and Experimental Station,  
Durham, New Hampshire, December 22, 1911.

## A RAPID AND ACCURATE METHOD FOR THE ANALYSIS OF WHITE METALS.

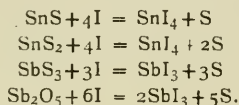
By J. C. BENEKER.

AFTER investigating and trying many methods for the analysis of bearing and type metals, I have devised a composite scheme which embodies the best features of other researches and several ideas which I believe are original. The method is rapid and at the same time accurate.

Dissolve  $\frac{1}{2}$  grm. of the fine drillings in a mixture of 25 cc. HCl + 5 cc. HNO<sub>3</sub> or 25 cc. HCl saturated with liquid bromine (not bromine water), warm on the steam-bath, and add about 1 grm. tartaric acid to hold up the antimony. Dilute with hot water to about 400 cc., and slowly add an excess of a solution of NaOH. Now add an excess (about 20 cc.) of a 10 per cent solution of Na<sub>2</sub>S. This is made by saturating half of a 10 per cent NaOH solution with H<sub>2</sub>S, and then adding the other half. Allow to settle, and filter by decantation a couple of times, using hot dilute

$\text{Na}_2\text{S}$  solution for washing. Transfer the precipitate to the filter, and wash with a hot dilute  $\text{Na}_2\text{S}$  solution several times. The residue consists of the sulphides of Cu, Pb, Fe, and Zn, while the filtrate contains Sn and Sb, also As if present (method of A. Rössing, *Journ. Chem. Soc. Ind.*, 1902, p. 191).

Dissolve the residue in  $\text{HNO}_3$ , and run down with  $\text{H}_2\text{SO}_4$  for the lead. The Cu, Fe, and Zn are determined as usual, the copper preferably by A. H. Low's iodometric method ("Technical Methods of Ore Analysis"). Add to the filtrate a small excess of HCl, and allow to settle on the steam-bath about an hour. Filter the precipitate, washing well with luke-warm water to remove all  $\text{H}_2\text{S}$ . Place the paper containing the sulphides in an Erlenmeyer flask. Add a measured excess of N/10 iodine solution, 30 to 50 cc. concentrated HCl, and about 2 grms. of tartaric acid. Never omit the tartaric acid, which serves to hold the antimony in solution. Insert a rubber stopper having a small swan-neck thistle tube in it to condense and retain any iodine vapours that might be evolved in heating. Heat the flask almost to boiling for a few minutes, whereupon the sulphides are changed to iodides:—



As will be seen, the tin is completely oxidised, whereas the antimony goes only to the triiodide form. Cool the flask, wash out the bulb tube, and dilute somewhat. Titrate the excess of iodine with a tenth-normal solution of sodium thiosulphate, using a starch indicator.

Now wash, or filter (if a sharper end-point is desired), into a beaker, neutralise with  $\text{Na}_2\text{CO}_3$ , and add an excess of powdered sodium bicarbonate. Now titrate with a tenth-normal solution of iodine (Mohr's method). In this alkaline solution the antimony triiodide is oxidised to the quinquivalent condition,  $\text{SbI}_3 + \text{I}_2 = \text{SbI}_5$ .

From this last titration the amount of antimony present can be calculated. Multiply the volume of iodine solution used in this titration by  $3/2$  and subtract this from the volume of iodine consumed in the first titration. This will give the volume of iodine consumed by the tin alone.

1 cc. 0.1 N iodine = 0.006 gm. Sb.  $\text{SbI}_3 + \text{I}_2 = \text{SbI}_5$ .  
1 cc. 0.1 N iodine = 0.00298 gm. Sn.  $\text{SnS}_2 + \text{I}_4 = \text{SnI}_4 + 2\text{S}$ .

This method of getting the tin and antimony by the titration of the sulphides is, as far as I know, original, and for it I can claim several advantages. One is that the antimony is put in just the stage of oxidation that is required for Mohr's titration. Another is that it does not matter in what condition of valency the sulphides are, even free sulphur does not interfere. This fact was ascertained by taking two samples of tin of 0.1 gm. each, dissolving one in concentrated HCl, forming  $\text{SnCl}_2$ , and the other in  $\text{HCl} + \text{HNO}_3$ , forming  $\text{SnCl}_4$ . Analysing as above gave almost identical results.

The separation of the insoluble sulphides from the tin and antimony can be made almost absolute by dissolving these sulphides of Cu, Pb, Fe, and Zn in hot HCl, and reprecipitating by means of NaOH and  $\text{Na}_2\text{S}$ . In this manner any traces of Sb or Sn that may have been retained by the first precipitate are removed and added to the main filtrate.

To test the above method of titrating the sulphides by means of iodine, I have weighed out samples of pure tin and run them through with this method, and have obtained the following close results, using the theoretical tin factor for the iodine:—

| Tin taken (grm.). | Tin obtained (grm.). |
|-------------------|----------------------|
| 0.0664            | 0.0669               |
| 0.0702            | 0.0705               |
| 0.0923            | 0.0922               |
| 0.1132            | 0.1135               |

To further test the method, known amounts of pure copper, lead, tin, and antimony were dissolved together, and tested in the above manner with the following result:—

|            | Taken (grm.). | Obtained (grm.). |
|------------|---------------|------------------|
| Copper ..  | 0.2995        | 0.2996           |
| Lead ..    | 0.2990        | 0.2997           |
| Tin ..     | 0.0946        | 0.0953           |
| Antimony.. | 0.0942        | 0.0936           |

—*Journal of Industrial and Engineering Chemistry*, iii., No. 9.

## QUICK COMBINATION METHODS IN SMELTER ASSAYS.\*

By A. T. FRENCH.

(Concluded from p. 75).

### THE SEPARATE DETERMINATIONS (continued).

#### Iron.

1. *Permanganate Method.*— $\text{KMnO}_4$ , 5.7 gm. per litre, 10 cc. = 0.1 Fe.

(a) *Reduction by Zinc.*—The sulphuric acid solution of the iron, which must be free from much HCl and even traces of nitrates, is warmed with 10 to 15 grms. of pure granulated zinc until a drop of the solution removed on a glass rod, and added to a drop of ammonium sulphocyanide solution on a white plate, remains colourless or only gives a faint pink tinge. The solution is then poured through a rapid filter into a flask, cooled, made up to about 500 cc. with cold distilled water, and titrated with standard permanganate. The reduction is best made in a solution containing only a little free acid; 10 cc. of 1 to 3 acid is usually enough, but more acid must be added if the reaction slackens before reduction is complete; 20 cc. more 1 to 3 acid should be added before titration.

(b) *Reduction by  $\text{H}_2\text{S}$ .*—The sulphuric acid solution of the iron, which must be free from much HCl (traces of nitrates do not interfere), is gassed with  $\text{H}_2\text{S}$  for ten minutes. Reduction is most rapid in faintly acid solutions—a large excess of acid should be nearly neutralised with  $\text{NH}_4\text{HO}$ ; the solution is boiled for about ten minutes, and tested by holding a piece of filter-paper saturated with lead acetate solution in the issuing steam. When no blackening of the paper occurs, the beaker is removed from the hot plate, and the solution filtered into a flask containing about 20 cc. dilute  $\text{H}_2\text{SO}_4$ , tested for ferric iron with ammonium sulphocyanide, cooled, made up to about 500 cc. with cold distilled water, and titrated with standard permanganate.

2. *Bicarbonate Method.*— $\text{K}_2\text{Cr}_2\text{O}_7$ , 4.4 gm. per litre, 20 cc. = 0.1 Fe. The iron in hydrochloric solution, containing about 5 cc. free HCl, should be warm and concentrated. It is carefully reduced with a solution of stannous chloride (15 grms. Sn, 350 cc. HCl per litre) added from a burette, and performing the reduction over a white plate. When colourless, two drops of the  $\text{SnCl}_2$  solution are added to make sure of having a slight excess, the solution is diluted with cold distilled water to about 300 cc., 10 cc. of a saturated solution of mercuric chloride are added (giving a white cloudy precipitate), and the solution titrated at once with standard potassium bichromate, using a 1 per cent solution of potassium ferricyanide as indicator. Spots of the indicator are placed on a white plate, and, after mixing each addition of the bichromate with the solution, a drop is withdrawn and added to one of the spots on the plate. A dark blue colour at first appears, gradually becoming fainter as the oxidation proceeds. Failure to colour after standing half a minute shows the end-point.

\* A Paper discussed at a Meeting of the Institution of Mining and Metallurgy, held at the Rooms of the Geological Society, Burlington House, Piccadilly, W., on Thursday, February 15th, 1912.



It is to be noted that a very small spot of ferricyanide should be taken for the final test.

The solutions of permanganate or bichromate are standardised by taking a weighed quantity of pure iron wire, or ferrous ammonium sulphate, and treating exactly as the assay. The pure iron wire usually supplied may be taken as containing 99.5 per cent pure iron, ferrous ammonium sulphate as containing one-seventh its weight pure iron.

Comparing the three methods, the  $H_2S$  permanganate is probably the safest, removing as it does most, if not all, sources of interference. The zinc permanganate is very commonly used; great care must be taken in testing the zinc used, and also that the solution is free from any trace of nitrates; the hydrates precipitated from a solution containing nitric acid carry down sufficient nitrate to interfere with the assay if simply dissolved in dilute  $H_2SO_4$ .

The  $SnCl_2$  bichromate method is the quickest, but requires more attention in reducing and titrating than does the permanganate; a good light is essential. The author finds that in most ores the small quantities of impurities carried down by the hydrate precipitate do not interfere with this method; it should be checked, however, against the  $H_2S$  permanganate.

EXPERIMENT II.—*Effect of Nitrates on the Iron Estimation.*—A solution was made up containing 0.1 gm. of iron (ferric) in 20 cc.

|                                                                                                  | Zn<br>(perman-<br>ganate).<br>Cc.        | $H_2S$<br>(perman-<br>ganate).<br>Cc. | $SnCl_2$<br>(bichro-<br>mate)).<br>Cc. |
|--------------------------------------------------------------------------------------------------|------------------------------------------|---------------------------------------|----------------------------------------|
| 1. 20 cc. required ..                                                                            | 10.0                                     | 10.0                                  | 20.0                                   |
| 2. 20 cc. + 5 cc. $HNO_3$ hydrates precipitated with $NH_4HO$ , dissolved in dilute $H_2SO_4$ .. | 12.7<br>15.3<br>precipitated in low bulk | 10.2<br>10.1                          | 20.0<br>hydrates dissolved in HCl      |
| 3. Same as 2, but hydrates precipitated twice .. ..                                              | 10.3<br>10.2                             | 10.1<br>10.1                          |                                        |

EXPERIMENT IIA.—*Effect of Cu, As, and Sb on the Bichromate Method.*—

4. 20 cc. of same solution + 0.05 gm. Cu—required 20.0 cc.
5. 20 cc. of same solution + 0.01 gm. Cu—bad titration; end reaction obscured 20.0 cc.
6. 20 cc. of same solution + 0.04 Sb and 0.01 As—required 20.2 cc.

#### Lead.

*Molybdate Method.*—Ammonium molybdate, 9.5 grms. per litre; 10 cc. = 0.1 gm. Pb. Sulphate of lead, thrown down, and filtered off as described in the analysis, is dissolved in a hot solution of ammonia acetate, slightly acidified with acetic acid. Spots of a freshly prepared solution of tannic acid are placed on a glazed porcelain plate, and the assay titrated hot with the standard molybdate, withdrawing a drop after each addition of the standard solution, and adding to a spot of tannic acid on the plate. The end-point is shown by the appearance of a yellow colour.

The basic sulphate of iron formed in the course of the analysis is soluble with difficulty; insufficient boiling after dilution and insufficient washing of the residue result in leaving some iron with the  $PbSO_4$ ; this gives a black colour with the tannic acid, spoiling the assay. The molybdate solution may be standardised on pure lead or on pure lead acetate, of which 0.183 gm. = 0.1 gm. Pb.

#### Lime.

*Permanganate Method.*— $KMnO_4$ , 5.7 grms. per litre; 20 cc. = 0.1 gm.  $CaO$ . Calcium oxalate, thrown down and filtered off as described in the analysis, will carry down

an appreciable amount of magnesium oxalate if much  $MgO$  is present. In this case it should be re-dissolved and re-precipitated.

The filter-paper containing the pure calcium oxalate precipitate is opened out, and the precipitate carefully washed back into the beaker with a jet of hot water. The paper is then placed on a large clock glass, and 10 cc. of dilute  $H_2SO_4$  (1 to 3) are poured on to it; after a minute or two the acid is poured off into the beaker containing the bulk of the precipitate, and the paper washed with hot water. A second treatment with acid and hot water will remove all the oxalate from the paper. The assay is brought to a boil, and when all the calcium oxalate has dissolved, the solution is diluted to about 300 cc. with hot water and titrated hot with standard permanganate.

#### Silica.

The insoluble obtained after attacking the ore with acids (after washing with ammonium acetate solution to free it from any traces of lead sulphate) is fused in a platinum dish or crucible with ten times its weight of fusion mixture ( $K_2CO_3 + Na_2CO_3$ ). After cooling, the melt is moistened with a few drops of water and 2 to 3 cc. of strong  $HCl$ , keeping carefully covered with a small watch-glass. When the action of the acid has nearly ceased the liquid is washed out into a porcelain capsule or casserole, and the process repeated. In this way the whole of the melt can be dissolved and transferred to the capsule in a few minutes, and the bulk of the solution should not exceed 100 cc. The capsule is placed on the hot plate and boiled to dryness—care must be taken to avoid spitting just at the moment when the salts are solidifying. When completely dry, as shown by the absence of condensing moisture on the cover-glass, the capsule is removed from the hot plate and allowed to cool. About 10 cc. of  $HCl$  are added, 50 to 100 cc. of hot water, and, after bringing to a boil to dissolve everything soluble, the residue is filtered off, washed, dried, ignited, and weighed as  $SiO_2$ .

A small amount of  $SiO_2$  remains in solution after this treatment, and can be recovered, by a second and third evaporation, to dryness. An allowance can be made for this off—

- 1 per cent on the  $SiO_2$  found, if more than 50 per cent.
- 2 per cent on the  $SiO_2$  found, if between 10 and 50 per cent.
- 4 per cent on the  $SiO_2$  found, if less than 10 per cent.

#### EXPERIMENT I2.—

1. Ore containing 95 per cent  $SiO_2$ —insoluble fused. Found in second evaporation,  $SiO_2$  0.007 gm.; repeated 0.005 gm.
2. Ore containing 27 per cent  $SiO_2$ —insoluble fused. Found in second evaporation,  $SiO_2$  0.003 = 0.02 gm.
3. Ore containing 9 per cent  $SiO_2$ —insoluble fused. Found in second evaporation,  $SiO_2$  0.002 = 0.002 gm.

#### Sulphur.

Barium chloride, 38 grms. per litre; 20 cc. = 0.1 gm. S. Either 0.5 or 1 gm. of ore, according to its richness in sulphur, is weighed into a 600 cc. beaker, 5 to 10 grms. of potassium chlorate are added, 5 to 10 cc. of water, and 10 to 15 cc. of strong  $HNO_3$ . The assay is heated, gently at first, and afterwards boiled down to near dryness. Ten cc. of 1-1 acetic acid and 5 to 10 grms. of ammonium acetate are added, about 250 cc. of hot water, the beaker is placed on the hot plate, brought to a boil, and the assay is ready to titrate.

Three cc. of  $HCl$  may be used instead of the acetic acid, and if the assay has been taken to complete dryness it gives better results, as basic sulphates are formed which

are soluble with difficulty in the acetic acid solution. The acetic acid seems to give a slightly clearer end reaction, but the difference is very small.

For the titration the solution should be boiling, and the beaker is kept over a small spirit-lamp. Spots of  $\text{BaCl}_2$  solution and of dilute  $\text{H}_2\text{SO}_4$  (about 9 cc. strong  $\text{H}_2\text{SO}_4$  per litre) are placed in parallel rows on a glass plate, supported about 6 in. above a dark surface. After each addition of  $\text{BaCl}_2$  a small portion of the solution is withdrawn by means of a glass tube, dropped into a filter, and from the filter on to two of the spots on the plate. At first a dense precipitate shows in the  $\text{BaCl}_2$  spot, gradually fading as the titration proceeds. Finally, a slight cloudiness appears in both spots, and when this is equal in intensity the assay is finished. A few more drops of  $\text{BaCl}_2$  may be added, and another test should show a distinctly denser precipitate in the  $\text{H}_2\text{SO}_4$  spot.

The  $\text{BaCl}_2$  solution may be standardised on pure ferrous ammonium sulphate; 0.613 gm. of this salt, containing 0.1 gm. of sulphur, is weighed out and treated exactly as the assay.

The above treatment with  $\text{HNO}_3$  and  $\text{KClO}_3$  leaves  $\text{BaSO}_4$  undecomposed; ores which contain this substance should be mixed thoroughly with about ten times their weight of a mixture of 1 part  $\text{Na}_2\text{CO}_3$  and 4 parts  $\text{ZnO}$ , placed in a porcelain crucible, and covered with a gm. or so of the mixture.

The crucible is heated to redness for a quarter of an hour, cooled, and the mass extracted with water and washed; the filtrate is acidified with  $\text{HCl}$ , adding about 3 cc. in excess, boiled a few minutes until all  $\text{CO}_2$  is expelled, and the sulphur estimated either gravimetrically or volumetrically. The volumetric method gives excellent results, the end-reaction in this modification being especially distinct.

Comparing methods, the following results were obtained:—

| Description of sample. | Gravimetric fusion with sodium carbonate. Per cent. | $\text{Na}_2\text{CO}_3 + \text{ZnO}$ . |                                |                                                       |
|------------------------|-----------------------------------------------------|-----------------------------------------|--------------------------------|-------------------------------------------------------|
|                        |                                                     | Gravimetric ignition. Per cent.         | Volumetric ignition. Per cent. | Volumetric $\text{HNO}_3 + \text{KClO}_3$ . Per cent. |
| Pyritic ore ..         | 26.53                                               | 26.7                                    | —                              | 26.5                                                  |
| Pyritic ore ..         | 30.56                                               | 30.7                                    | —                              | 30.5                                                  |
| Pyritic ore ..         | —                                                   | 31.1 <sup>a</sup>                       | 31.0                           | 31.2                                                  |
| Matte ..               | —                                                   | 22.0 <sup>a</sup>                       | 21.8                           | 21.8                                                  |
| Roasted ore..          | —                                                   | 5.7                                     | —                              | 5.6                                                   |

The end-point may seem a little doubtful at first, but practice will enable it to be determined with certainty within 0.2 cc., and very concordant results obtained. The following results were obtained in the author's laboratory on daily samples of roasted ore, checked by an average weekly sample:—

|                            |      |                  |                  |                  |                  |
|----------------------------|------|------------------|------------------|------------------|------------------|
| Average of daily samples.. | 7.67 | 7.2 <sup>b</sup> | 8.2 <sup>a</sup> | 8.6 <sup>a</sup> | 9.0 <sup>a</sup> |
| Assay of average samples   | 7.6  | 7.3              | 8.3              | 8.6              | 8.9              |

### Zinc.

**Ferrocyanide Method.**—Potassium ferrocyanide, 43.1 grms. (10 cc.) per litre = 0.1 gm. Zn. The ammoniacal filtrate from the iron which will contain ammonium oxalate of lime has been estimated, and may contain copper, antimony, &c., but not manganese (Experiment 6) is acidified with  $\text{HCl}$ , adding 5 cc. in excess.  $\text{H}_2\text{S}$  is passed for five to ten minutes, and the solution boiled until  $\text{H}_2\text{S}$  is expelled. It is then titrated with standard potassium ferrocyanide, using spots of uranium acetate solution (8 per cent) on a white plate as indicator. The temperature of the solution may be near boiling if oxalates are absent, but if present the temperature should not exceed 30° C. (Experiment 8).

The thorough gassing of the solution before titration is very important, and should never be omitted.

## THE VOLUMETRIC CHROMATE DETERMINATION OF LEAD.

By JOHN WADDELL.

IN the *Transactions of the American Institute of Mining Engineers*, 1905, xxxv., 359, Mr. H. A. Guess gives a method for determining lead in ores. Though it can be used for nearly all kinds of ores, it is most satisfactory in just those cases for which the results obtained by the molybdate method are least reliable, namely, with ores poor in lead and containing a large amount of calcium carbonate.

Guess claims that the method is easily carried out, and I understand that it is employed at the Trail Smelter in British Columbia.

It does not seem, however, to have become at all general. I have not found it in any of the books on quantitative analysis, nor have I seen it described in any of the chemical periodicals. Guess describes the method as follows:—

To the ore charge of from 1 to 5 grms. in a 250 cc. flask add from 3 to 5 cc. of strong nitric acid and 15 cc. of strong hydrochloric acid; digest until everything is in solution and the excess of acid has been reduced to about 8 cc. The whole operation on the hot plate requires but fifteen minutes. The flask is then removed, and slightly diluted ammonia is added slowly in slight excess, the neutralising action being sufficiently vigorous to render the contents of the flask quite hot. Acetic acid of 80 per cent strength is then added slowly, the flask being shaken vigorously until the smell indicates a decided excess of acetic acid. Then 5 cc. of strong ammonium acetate are added to insure the solution of any lead compounds remaining undissolved by the ammonium acetate already formed in the flask.

If the ore contains no antimony or separated gelatinous silica, and if the siliceous residue in the bottom of the flask is only in slight amount (as is usual with heavy lime ores or with concentrates) add to the hot undiluted and unfiltered solution an excess—about 10 cc.—of a 10 per cent potassium chromate solution. Under these conditions the bulk of the contents of the flask will not exceed 50 cc., and after shaking and letting the precipitated lead chromate settle for about five minutes the contents are filtered through an 11 cm. filter of any fairly rapid and close paper. If these directions are carried out the lead chromate will be quite granular, and will show no tendency to run through. The precipitate in the flask and on the filter is washed several times with hot water containing about 0.5 per cent of acetic acid until free from soluble chromates. The funnel with the filter is then set over the original flask and hot dilute hydrochloric acid (1 : 1) poured through the filter, dissolving the lead chromate. Further additions of hydrochloric acid are made if necessary, and all lead chromate is dissolved from the filter; then it is washed with warm water until free from chromate.

The original flask now contains nothing but the hydrochloric acid solution of the lead chromate and the washings, which, after adding a small crystal from 0.5 to 2 grms. in weight of potassium iodide, is titrated direct with standard "hypo" solution whose value is known in terms of lead, the most suitable strength being that in which 1 cc. is equal to 5 mgrms. of lead. In this operation, by using only a small quantity of potassium iodide and having the solution fairly strong with hydrochloric acid (about 50 cc. of hydrochloric acid 1 : 1 in a total of 200 cc. of solution), and somewhat warm, any tendency of the lead to form yellow scales of lead iodide, and thus somewhat obscure the end reaction with starch, is completely checked, and the end reaction is sharp.

The sharpness of the end-point with starch, as opposed to the indistinctness of the end-point in the molybdate method, is given as one of the special features.

Students working in my own and other laboratories



have found difficulties with this method. Sometimes the blue colour of the starch disappeared on addition of thiosulphate, only to come back in a minute or two; in other cases the precipitate of lead chromate seemed not to be washed free from soluble chromate in the course of an hour or more; sometimes even when no error was visible the results were not concordant. Owing to the difficulties experienced by my students last winter, I ran through a couple of determinations of an ore myself, and obtained 23.61 per cent and 24.20 per cent, a difference of half a per cent.

Since the method is especially interesting from an instructional point of view, I decided to investigate the points of difficulty. I may say incidentally that treatment of the ore with hydrochloric acid before the addition of nitric acid is to be recommended, since it lessens the tendency to form a globule of sulphur which may enclose some lead.

The effect of varying the strength of acid used in the titration was first tried. To about 10 cc. of a solution of chromate (9.4 grms. per litre) 200 cc. of a mixture of strong hydrochloric acid and water, in which the acid varied between 5 cc. and 100 cc., were added, and after addition of potassium iodide the iodine was titrated with thiosulphate. With small quantities of acid the blue colour of the starch, after being first discharged, came back after a minute or two. With 5 cc. of acid the colour was discharged and reproduced several times, and even with 20 cc. the colour came back once. It seems that there should be at least 25 cc. of acid present.

Titration in which the chromate had been heated with acid for varying lengths of time between 60° and 80° C. showed in general partial decomposition, though the variations were not always of the order that might be expected.

As there is evidently a time reaction between the chromate, hydrochloric acid, and potassium iodide, the effect of varying amounts of iodide, up to 1 gm., were tested. The most concordant results were obtained by using 1 gm. of iodide, and by running in the thiosulphate drop by drop, about three drops a second, 1 cc. of chromate in that case being equal to 1.968 cc. and 1.976 cc. of thiosulphate in duplicates. In this set of experiments 25 cc. of acid and 175 cc. of water were added to 15 cc. of a chromate solution measured by a pipette.

One source of error in the method was found to be the solubility of lead chromate in the 0.5 per cent acetic acid used for washing. The addition to 50 cc. of this acid of two or three drops of a solution containing less than 1 per cent of chromate rendered its solvent action almost nil, and hence the acid may be used till nearly all the soluble chromate is washed out, but finally pure water is required.

In order to avoid possible error from setting free chlorine by the use of half and half hot hydrochloric acid, I dissolved the lead chromate with a cold mixture of 25 cc. of hydrochloric acid and 75 cc. of water, washing alternately with this mixture and with cold water. From time to time 5—10 cc. of hot water were used for the more perfect dissolution of the lead chloride.

The precipitate having been all dissolved and washed into the flask as Guess describes, the liquid was made up to about 200 cc., and 1 gm. of potassium iodide was added, followed immediately, to avoid loss of iodine, by thiosulphate from the burette at the rate of two or three drops a second. After the brown colour had nearly disappeared and had given place to a dark green, starch was added and the thiosulphate run in, a few drops at a time, with vigorous shaking. When the blue colour was nearly discharged I added 10 cc. of strong hydrochloric acid and heated the flask to 40° C., after which two or three drops of thiosulphate were sufficient to bring the clear green colour of the chromic salt, which constitutes the end-point.

The following results were obtained, using the modified method:—

Twenty-five cc. of a solution of pure lead containing

0.150 gm. of lead required in duplicate determinations 30.65 and 30.51 cc. of thiosulphate. A student who made a check determination used 30.50 cc. The average is 30.55 cc.; or 1 cc. thiosulphate equals 0.00491 gm. lead.

A solution of ore was made, such that 25 cc. would require somewhere about 30 cc. of thiosulphate. In four determinations the figures obtained were 28.73, 29.25, 29.25, and 29.25 cc. A student made a check determination, dissolving the lead chromate in 50 cc. of 1 : 1 cold hydrochloric acid, and using half a gm. of chromate. He required 29.04 and 28.97 cc. of thiosulphate.

Afterwards I made four determinations, taking half a gm. of ore, and required 28.30, 28.40, 28.28, and 28.30 cc. of thiosulphate. The lowest and highest figures give respectively 27.76 and 27.88 per cent of lead.

The difference between the Guess method of solution of lead chromate and the one which I adopted was tested by sprinkling basic lead chromate upon two filters and dissolving one quantity with nearly boiling 1 : 1 acid, and the other in the manner I have described. In the first case 1 cc. thiosulphate = 0.01516 gm. chromate; in the second 1 cc. thiosulphate = 0.01446 gm. chromate.

Assuming that the second determination was correct, the 0.4336 gm. of chromate used in the first case should have required 29.99 cc. of thiosulphate instead of 28.60 cc., which was actually used. With starch iodine paper chlorine can be readily detected when hot 1 : 1 hydrochloric acid is put upon lead chromate.

In the presence of large quantities of iron, say, 20 per cent, the tendency to form basic acetate gives difficulty in dissolving the lead. Of course any ferric acetate precipitated along with lead chromate is fatal. Guess points out that the presence of antimony, bismuth, silver, or gelatinous silica interferes with the process, but says that if the lead is first changed to sulphate, and after separation from the soluble sulphates, dissolved in ammonium acetate as for the molybdate determination, the rest of the process may be carried out as before. In this case the only advantage in the chromate method is its delicacy; it takes a longer time, but duplicate determinations should check within a tenth of 1 per cent, and often do check within two or three hundredths.

I wish to acknowledge help given by several students, particularly by Mr. H. Bradley and Mr. W. Agassiz.—*Journal of Industrial and Engineering Chemistry*, iii., No. 9.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

Ordinary Meeting, February 22nd, 1911.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

THE Bakerian Lecture was delivered by Prof. H. L. CALLENDAR, M.A., LL.D., F.R.S., "On the Variation of the Specific Heat of Water, Investigated by the Continuous Mixture Method."

(Summary).

The experiments of Callendar and Barnes on the variation of the specific heat of water between 0° and 100° C. by the continuous electric method (*Phil. Trans. Roy. Soc.*, A, 1902) with platinum thermometers, agreed with those of Lüdin by the method of mixture with mercury thermometers more closely than with those of any previous observers, but gave results nearly 1 per cent lower than Lüdin's over the range 60° to 90° C. Within the last year the results of Lüdin have been very closely reproduced by W. R. and W. E. Bousfield (*Phil. Trans.*, A, 1911), employing a Dewar calorimeter electrically heated by a mercury resistance, the rise of temperature being observed

by means of mercury thermometers standardised to  $0.01^{\circ}$  C. every  $5^{\circ}$ .

The present investigation was designed to verify the results of Callendar and Barnes by a new and independent method, called the continuous mixture method, in which a current of water at a steady temperature  $t_1$  in the neighbourhood of  $100^{\circ}$  C. is passed through an arrangement of concentric tubes, called a "heat-exchanger," emerging at a measured temperature  $t_2$  in the neighbourhood of  $70^{\circ}$  C. After being cooled to a measured temperature  $t_3$  in the neighbourhood of  $30^{\circ}$  C., the same current is passed through the heat-exchanger again, abstracting heat from the hot current by conduction, without actual mixture, and emerging finally at a measured temperature  $t_4$  in the neighbourhood of  $60^{\circ}$  C. By a suitable arrangement of the flow-tubes the external heat-loss can be reduced almost to a vanishing quantity (20 to 100 times smaller than in the electric method) without the employment of vacuum-jackets or elaborate precautions in lagging. The flow can be varied over a very wide range (20 to 1) without materially affecting the distribution of temperature; and, since the hot and cold currents are the same, a comparatively rough measurement of the current suffices for the determination of the heat-loss.

The water equivalent of the exchanger is immaterial provided that the conditions are fairly steady; and there is no possibility of uncertain loss by evaporation as with an open calorimeter. The accuracy attainable is limited chiefly by the temperature readings, which are taken with platinum thermometers to  $0.001^{\circ}$ , equivalent to 1 in 30,000 of the heat-exchanger. Since the loss of total heat by the hot current is equal to the gain of total heat by the cold current *plus* the small external heat-loss, the experiment gives directly the ratio of the mean specific heat from  $t_2$  to  $t_1$  ( $70^{\circ}$  to  $100^{\circ}$  C.) to the mean specific heat from  $t_3$  to  $t_4$  ( $30^{\circ}$  to  $60^{\circ}$  C.). The results of about 150 experiments by this method, in which the conditions as to flow and heat-loss were varied as widely as possible, were such as to confirm the continuous electric method over this range of temperature to less than 1 in 5000, whereas the discrepancy from Lüdén's formula exceeded 1 in 200, which is more than the whole variation of the specific heat over the range  $10^{\circ}$  to  $80^{\circ}$  C. according to the continuous electric method.

A single formula has been found to represent the variation of the specific heat  $s$  according to the continuous electric and mixture methods over the range  $0^{\circ}$  to  $100^{\circ}$  C. The formula is as follows:—

$$s = 0.98336 + 0.504'(t + 20) + 0.0084(t/100) + 0.0090(t/100)^2,$$

in terms of the specific heat at  $20^{\circ}$  C. taken as unity, and in terms of the scale of the temperature  $t$  deduced from the platinum scale  $pt$  by means of the standard difference-formula—

$$t - pt = 1.50t(t - 100) \times 10^{-4}.$$

The same formula for the specific heat also represents the most probable reduction of Regnault's experiments over the range  $110^{\circ}$  to  $190^{\circ}$  C.

Papers were also read as follows:—

"Short Index to Reports of Physical Observations—Electric, Magnetic, Meteorological, Seismological—made at Kew Observatory." By Dr. C. CHREE, F.R.S.

"Velocities of Ions in Dried Gases." By R. T. LATTEY, M.A., and H. T. TIZARD, M.A.

The authors have determined the velocities of positive and negative ions in dried hydrogen and carbon dioxide. The results obtained are completely parallel to those already obtained in a previous investigation on air (R. T. Lattey, *Proc. Roy. Soc.*, lxxiv., 173).

The velocity of positive ions is but little affected by the presence of moisture in the gas, and is proportional to the force ( $x$ ), and inversely proportional to the pressure ( $p$ ).

The same relation approximately holds good for the velocity of negative ions in moist gases. When the gas is extremely dry, however, the negative ions are apparently

very easily deprived of their customary envelope. Their velocity therefore does not increase proportionately to  $x/p$ , but at a very much greater rate.

"Observation by means of a String Electrometer of Fluctuations in the Ionisation produced by  $\gamma$ -Rays." By Prof. T. H. LABY, B.A., and P. W. BURBIDGE, B.Sc.

The authors claim to have demonstrated that there are fluctuations in the ionisation produced by  $\gamma$ -rays, and have worked out the technique for future experiments, where the absolute amount of the fluctuation is very small. Further experiments are necessary before the experiments can be said to support either a corpuscular or pulse theory of  $\gamma$ -rays.

"Wave-problem of Cauchy and Poisson for Finite Depth and Slightly Compressible Fluid." By F. B. PIDDUCK, M.A.

The paper is in some respects a completion of a former one on the propagation of a disturbance in a fluid under gravity. The solution of the two-dimensional Cauchy-Poisson problem for finite depth is worked out numerically, the effect of limiting the depth being very considerable. The fact is brought to light that up to a certain point a limitation of the depth causes an increase in the elevation at a given point for a short interval of time after the beginning of the motion. The wider question presents itself as to the sense in which the initial disturbance can be said to be confined to a definite portion of the fluid. Difficulties connected with the assumption of incompressibility are avoided by considering a heavy compressible fluid. The application of an extension of Fourier's theorems, due to Orr, gives the solution of the problem of such a fluid held with every part in a given state of compression and then released, the free surface being maintained at constant pressure. The known formulae for incompressible fluid for both finite and infinite depth follow as limiting expressions, and it is possible to detect the existence of an advancing wave-front when the compressibility is different from zero.

The following papers, originally announced for the Meeting of February 15th, which was adjourned on account of the death of Lord Lister, were taken as read:—

"Alleged Specific Instance of the Transmission of Acquired Characters.—Investigation and Criticism." By Dr. T. GRAHAM BROWN.

"Further Experiments on the Cross-breeding of Two Races of the Moth *Acidalia virgularia*." By W. B. ALEXANDER, B.A.

"Effects of Castration and Ovariectomy upon Sheep." By F. H. A. MARSHALL.

"Causes and Prevention of Miners' Nystagmus." By Dr. T. L. LLEWELLYN.

"The Stomatograph." By W. LAWRENCE BALLS.

The Stomatograph is a self recording instrument adapted from Mr. Francis Darwin's *Porometer* (F. Darwin and D. Pertz, *Proc. Roy. Soc.*, B, lxxiv.). In these instruments the aperture of the stomata is estimated by the rate at which air under constant pressure can be forced through the stomata of a living leaf. In the stomatograph the current of air is produced by forcibly sinking a minute bell-jar in a beaker of water or other fluid. The air in the bell is thus compressed, and since it communicates with a chamber luted on to the experimental leaf, a flow of air is set up through the stomata. When the bell has sunk to a certain point an electric release causes it to rise, and at the same time makes a mark on a rotating drum. Thus if the stomata are widely open there is a rapid fall or rise of the bell-jar, and the marks on the drum are close to one another, whereas with nearly closed stomata the marks are relatively wide apart.

A five days' record of the opening and closing of the stomata of the cotton plant in Egypt is given, showing the stomata wide open during bright sunshine. The author



has elsewhere shown that during this part of the day no growth occurs, and there is evidence that the apparent waste of water then occurring is of importance as keeping the leaves cool, since when transpiration is artificially checked the leaves are rapidly injured or even killed by the high temperature.

"Composition of the Blood Gases during the Respiration of Oxygen." By G. A. BUCKMASTER and J. A. GARDNER.

A number of analyses were made of the blood of cats respiring (1) air, (2) oxygen for periods of one to two hours.

The average composition in cc. per 100 cc. of arterial blood for cats breathing air was as follows (mean of thirteen experiments) :—

|                         |       |
|-------------------------|-------|
| Total gas .. .. .       | 53.76 |
| CO <sub>2</sub> .. .. . | 38.43 |
| O <sub>2</sub> .. .. .  | 14.22 |
| N .. .. .               | 1.12  |

The percentage saturation of hæmoglobin with oxygen was 83.

For cats breathing oxygen the mean values by thirteen experiments was as follows :—

|                         |       |
|-------------------------|-------|
| Total gas .. .. .       | 53.79 |
| CO <sub>2</sub> .. .. . | 38.65 |
| O <sub>2</sub> .. .. .  | 14.93 |
| N .. .. .               | 0.16  |

The average percentage saturation of hæmoglobin with oxygen was 89.6

From their experiments the authors conclude that the inhalation of oxygen does not materially augment either the quantity of this gas or the quantity of carbon-dioxide in the blood.

#### CHEMICAL SOCIETY,

*Ordinary Meeting, February 15th, 1912.*

Prof. PERCY F. FRANKLAND, LL.D., F.R.S., President,  
in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Arthur Leslie Bartow, Kingscot, Ruislip; Ernest Gower Bryant, 100, Burlington Street, Manchester; Charles Rugeley Burv, B.A., Ellfield, Wotton-under-Edge, Glos.; James Grainger Hill, 124, Borneo Street, Walsall; John Owen Hughes, B.Sc., University College of N. Wales, Bangor; Edgar Dingle Jones, 3, Neville Road, Waterloo, Liverpool; Richard Arnold Seymour-Jones, M.Sc., Lyddon Hall, Virginia Road, Leeds; William Thornion Lucas, B.A., 62, Mowbray Road, South Shields; Bawa Kartar Singh, B.A., Dacca College, Dacca, Bengal.

The PRESIDENT made the following announcements :—

1. That the Council had proposed the following gentlemen as Honorary and Foreign Members, and that a ballot for their election would take place at the Ordinary Scientific Meeting of the Society to be held on Thursday, March 7th: Prof. Philippe A. Guye (Geneva), Prof. Thomas Burr Osborne (Newhaven, Conn.), Prof. Paul Walden (Riga), Prof. Richard Willstätter (Zurich).

2. That the following changes in the Officers and Council were proposed by the Council :—  
*Vice-Presidents to retire*—Prof. J. Norman Collie and Prof. James Walker.

*Secretary to retire*—Prof. G. T. Morgan.

*Ordinary Members of Council to retire*—Prof. J. B. Cohen, Mr. C. F. Cross, Mr. C. E. Groves, and Dr. A. E. H. Tutton.

*As President*—Prof. Percy F. Frankland.

*As Vice-Presidents who have filled the Office of President*—Prof. H. E. Armstrong, Prof. A. Crum Brown, Sir William Crookes, Sir James Dewar, Prof. H. B. Dixon,

Dr. A. G. Vernon Harcourt, Prof. R. Meldola, Dr. H. Müller, Prof. W. Odling, Sir William Ramsay, Prof. J. Emerson Reynolds, the Right Hon. Sir Henry E. Roscoe, Sir Edward Thorpe, and Sir William A. Tilden.

*As Treasurer*—Dr. Alexander Scott.

*As Hon. Secretaries*—Prof. Arthur W. Crossley and Dr. Samuel Smiles.

*As Foreign Secretary*—Dr. Horace T. Brown.

*As Vice-Presidents*—Dr. G. T. Beilby, Dr. M. O. Forster, Prof. A. Liversidge, Prof. E. J. Mills, Prof. G. T. Morgan, and Prof. W. J. Pope.

*As New Ordinary Members of Council*—Dr. H. G. Colman, Dr. A. Harden, Dr. T. M. Lowry, and Dr. E. J. Russell.

3. That Prof. P. F. Frankland had been appointed to represent the Society at the funeral of the late Lord Lister, P.C., O.M., F.R.S.

4. That with the object of keeping the Library as up to date as possible, the Council would especially welcome the gift of works written by Fellows of the Society.

Dr. F. B. Power, Prof. J. Millar Thomson, and Dr. Samel Rideal were elected Auditors to audit the Society's Accounts.

A ballot for the election of Fellows was held, and the following were subsequently declared elected :—Hilmar Johannes Backer; Clement William Bailey, M.Sc.; Fred Barrow, M.Sc., Ph.D.; Ernest Arthur Bearder, M.Sc.; G. bbs Blackstock, B.A.; James Ewart Bridge, B.Sc.; David Brownlie, B.Sc.; Thomas Alfred Brunjes; Sidney Waterfield Bunker, B.Sc.; William Thomas Clarke, B.Sc.; Tom Peach Colclough, M.Sc.; Frederic Fernandez Curtis; Surendranath De; Thomas Sharp Dick; Harold Forster Dodson; John Duncan; Rowland Holliday Ellis; Wilfred James Fleet, Cornelius Durham Garbutt; Ernest George Gaul, M.Sc.; Jyotish Chandra Ghosh; Richard Ernest Gibbins; Thomas Sidney Haines; Isidor Morris Heilbron, Ph.D.; Charles James; William McMillan; James William McMyn; Herbert Middleton, M.Sc.; Pestanji Manekji Modi, B.A.; Ernest Meyer Myers; William Johnson Smith Naunton, B.A., B.Sc.; Richard Gillies Neilson; James Pettigrew Ogilvie; John Wilfred Parks; Rupert William Pope, B.Sc.; Howard Vincent Potter; William Raitt; Edgar Alexander Rayner, B.Sc.; Alfred Reginald Roberts; Walter Morrell Roberts, M.Sc.; Bertram James Smart, B.Sc.; Henry Edgar Smith, M.Sc.; Richard Smith; Percy Rudolph Strivens; Cecil Hamersley Waldron; Forsyth James Wilson, D.Sc., Ph.D.; John Charles Withers, Ph.D.; John Kerfoot Wood, D.Sc.

Of the following papers, those marked \* were read :—

\*25. "*Perhalides of Diphenyliodinium Iodide.*" By MARTIN ONSLOW FORSTER and JOHANNES HEINRICH SCHAEPLI.

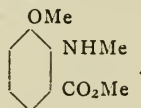
The *tetrachloride*, *dichloride*, *iodochloride*, *diiodide*, and *iodobromide* of diphenyliodinium iodide were described, together with the *diiodide* and *di-iodide* of diphenyliodinium bromide, and the *diiodide* and *iodide* of diphenyliodinium chloride.

#### DISCUSSION.

Sir WILLIAM TILDEN said that this paper interested him because the preparation and properties of certain periodides had been the subject of the first communication he ever made to the Chemical Society. It was curious to notice that the problem presented by the exterior atoms of halogen in these compounds appeared to be in nearly the same position as it was forty years ago. He inquired whether the new compounds presented in the crystalline form the power of polarising ordinary light exhibited by so many of those already known, as, for example, the substance formerly called "herapathite."

\*26. "*The Constitution and Synthesis of Damascenine, the Alkaloid of Nigella damascene.*" By ARTHUR JAMES EWINS.

Damascenine has been proved by synthesis to be the methyl ester of 2-methylamino-3-methoxybenzoic acid,—



It thus possesses the composition  $C_{10}H_{11}O_3N$ , differing from the formula originally suggested by Schneider (*Pharm. Centr.-h.*, 1890, xxxi., 173) only by having two hydrogen atoms less. The formula  $C_9H_{11}O_3N$ , assigned to this alkaloid by Pommerehne (*Arch. Pharm.*, 1900, ccxxxviii., 531), and the betaine-like constitution suggested by Keller (*Arch. Pharm.*, 1908, ccxlvii., 1) are therefore without foundation, the "damascenine hydrochloride" of these workers being a mixture of the hydrochlorides of damascenine and damascenic acid.

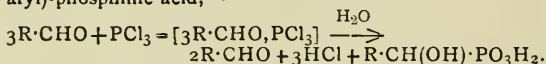
\*27. "The Action of Ozone on Cellulose." By MARY CUNNINGHAM and CHARLES DORÉE.

Ozone (concentration 1 to 2 per cent) rapidly attacks cotton, forming a cellulose peroxide and an acid derivative, together with some carbon dioxide. The peroxide is decomposed at  $80^\circ$ . The acid may be removed by boiling with water or digestion with  $N/10$  alkali; the neutral fibre residue then obtained is an oxycellulose. The acidity and the amount of carbon dioxide produced during treatments varying from one to twenty hours have been measured, and the constants of the oxycellulose determined and compared with typical oxycelluloses.

The lignocellulose is not appreciably affected unless water is present. In that case it is oxidised, giving carbon dioxide, acetic and formic acids, and complex non-volatile acids which yield furfuraldehyde. Quantitative measurements of the progressive action of the ozone show that the lignone group is rapidly attacked in the first three hours, after which the action becomes slower, the residue being then oxidised uniformly. The lignin reactions cease when the loss of weight is about 33 per cent. Direct evidence of ozonide formation has not been obtained, although the formation of acetic and formic acids appears to be due to the decomposition of some product formed, in the first instance, by the action of ozone.

\*28. "Hydroxymethylphosphinic Acid and some Homologues." By HAROLD JAMES PAGE.

Fossek found that when an aldehyde (3 mols.) and phosphorus trichloride (1 mol.) were mixed, an unstable viscous oil resulted. When this was treated with water, two-thirds of the original aldehyde was regenerated, together with hydrogen chloride and  $\alpha$ -hydroxy-alkyl (or aryl)-phosphinic acid,—



Fossek's results have been confirmed, and the above reactions further examined. An attempt to distil the intermediate oil in a vacuum was fruitless. An explanation of the mechanism of the reaction and of the constitution of the intermediate oil was, however, advanced.

The first member of the series, namely, hydroxymethylphosphinic acid, was not prepared by Fossek. It has been obtained in a 93 per cent yield by the action of trioxymethylene on phosphorus trichloride, and it has been shown that it is also produced by the action of formaldehyde on phosphorus trichloride, although not in a pure state.

Hydroxymethylphosphinic acid,  $CH_2(OH) \cdot PO_3H_2$ , is in most respects similar to the other members of the series; as typical member, however, it exhibits certain anomalous properties.

#### DISCUSSION.

Mr. C. HOLLINS drew attention to the ethereal oxygen linking in one of the suggested intermediate compounds, and asked the author whether the acids showed any tendency to form inner anhydrides.

Dr. J. F. SPENCER pointed out that all the compounds described, except the first member of the series, contained asymmetric carbon atoms, and asked whether the author had any evidence of the existence of the two optically active isomerides in any of the compounds examined.

Mr. PAGE replied that no indication of the formation of an inner anhydride had been observed, and that he proposed to attempt the resolution of some of the acids.

29. "Chemical Examination of Scammony Root and of Scammony." By FREDERICK BELDING POWER and HAROLD ROGERSON.

The material employed for this investigation consisted of Levant scammony root (from *Convolvulus scammonia*, Linné), and the product known as scammony, or "virgin scammony," the latter having been obtained directly from Smyrna.

The scammony root yielded 9.65 per cent of resin, 97 per cent of which was soluble in ether, whereas the gum-resin, scammony, contained 83.1 per cent of resin, which was completely soluble in ether. The specific rotatory power of the two crude resins was  $[\alpha]_D -20.20^\circ$  for that obtained from the root, and  $[\alpha]_D -21.15^\circ$  for that from scammony.

For a complete examination of the root, 50.35 kilograms of the ground material were extracted with hot alcohol. The resulting extract, when distilled in a current of steam, yielded a very small amount of an essential oil. From the portion of the extract which was soluble in water the following substances were isolated:—Scopoletin,  $C_{10}H_8O_4$ ; 3:4-dihydroxycinnamic acid,  $C_9H_8O_4$ ; and a small amount of sucrose. The aqueous liquid contained, furthermore, a quantity of dextrose. The portion of the alcoholic extract which was insoluble in water consisted of a resin which possessed the above mentioned characters.

The resins obtained from scammony root and from scammony respectively, sometimes designated as "scammonin," are very similar in many respects, but not perfectly identical. On the other hand, the resin of scammony root was found to differ very considerably from that obtained from the root of *Ipomoea orizabensis* (*Trans.*, 1912, ci., 1), which has received the appellation of "jalapin." Both of these resins consist of exceedingly complex mixtures, and their components are not entirely glucosidic.

30. "Experiments on the Walden Inversion. Part VIII.  $\alpha$ -Amino- $\alpha$ -phenylpropionic Acids." By ALEX. MCKENZIE and GEORGE WILLIAM CLOUGH.

*dl*- $\alpha$ -Formylamino- $\alpha$ -phenylpropionic acid was resolved into its optically active components by cinchonidine and quinine, and the amino-acids were prepared by hydrolysing the active formyl compounds with hydrobromic acid. The following values were obtained:—

*d*- $\alpha$ -Formylamino- $\alpha$ -phenylpropionic acid,  $[\alpha]_D +91.9^\circ$  in ethyl-alcoholic solution.

*l*- $\alpha$ -Formylamino- $\alpha$ -phenylpropionic acid,  $[\alpha]_D -91.6^\circ$  in ethyl-alcoholic solution.

*d*- $\alpha$ -Amino- $\alpha$ -phenylpropionic acid,  $[\alpha]_D +70.0^\circ$  in aqueous solution.

*l*- $\alpha$ -Amino- $\alpha$ -phenylpropionic acid,  $[\alpha]_D -69.5^\circ$  in aqueous solution.

Complete racemisation took place with the formation of *r*-atrolactic acid when the amino-group in the active amino-acids was displaced by the hydroxy-group by means of nitrous acid. Again, when the *d*-amino-acid was acted on by a mixture of fuming hydrochloric acid and sodium nitrite, the racemisation was practically complete.

31. "Preparation of the Nitrites of the Primary, Secondary, and Tertiary Amines." (Part I.) By PANCHANAN NEOGI.

A detailed description was given of the preparation of the nitrites of the primary, secondary, and tertiary amines, a preliminary account of which has already appeared (*Proc.*, 1911, xxvii., 242).



32. "Nitrites of the Mercurialkyl- and Mercurialkylaryl-ammonium Series." By PRAFULLA CHANDRA RAY, JITENDRA NATH RAKSHIT, and RASIK LAL DATTA.

By the interaction of mercuric nitrite and the alkyl- and alkylaryl-amines the following mercury-substituted alkyl- and alkylaryl-ammonium nitrites have been obtained:—Trimercuridibutylammonium nitrite (compare *Trans.*, 1911, xcix., 1972), mercurisobutylammonium nitrite, mercuribenzylammonium nitrite, mercuridiphenylammonium nitrite, mercuridi-p-tolylammonium nitrite, mercuridibenzylmethylammonium nitrite, mercuridibenzylethylammonium nitrite, mercuridipyridinium nitrite, mercuridiquinolinium nitrite, mercuridinaphthylammonium nitrite, and mercuripiperazinium nitrite.

33. "Nitrites of the Alkylammonium Series. Part IV. isoButyl-, Diethyl-, Dipropyl-, and Tripropyl-ammonium Nitrites." By PRAFULLA CHANDRA RAY and JITENDRA NATH RAKSHIT.

By the usual method, namely, double decomposition between the corresponding substituted ammonium chloride and silver nitrite, the above nitrites have been obtained. Of these, isobutylammonium nitrite and tripropylammonium nitrite are liquids. Diethyl- and dipropyl-ammonium nitrites are crystalline compounds, and can be sublimed in a vacuum without decomposition.

34. "The Hydrolysis and Saponification of Esters of Saturated and Unsaturated Acids." By THOMAS WILLIAMS and JOHN JOSEPH SUDBOROUGH.

The hydrolysis of the ethyl esters of propionic, acrylic, n-butyric, crotonic,  $\beta$ -phenylpropionic, and cinnamic acids by means of dilute hydrochloric acid have been determined at 20°, and also the saponification values of the same esters by means of dilute barium hydroxide.

The results indicate that an unsaturated ester is not nearly so quickly hydrolysed as its saturated analogue by means of dilute hydrochloric acid. With the three pairs of esters examined, the constant for the saturated ester is about thirty times as great as that for the unsaturated.

The differences in the saponification values are not so marked, and when the unsaturated acid is much stronger than the saturated, as is the case with acrylic and propionic acids, the ester of the unsaturated acid can be saponified more rapidly than its saturated analogue.

35. "Investigations on the Dependence of Rotatory Power on Chemical Constitution." (Preliminary Note). By ROBERT HOWSON PICKARD and JOSEPH KENNON.

The authors are continuing their investigations, and now find that the method (see *Trans.*, 1911, xcix., 45) of resolving racemic alcohols into their optically active components can be applied to many types of secondary alcohols. For the purposes of these investigations it has already appeared desirable to contrast the properties of series of very closely allied compounds. It is not proposed therefore to publish details of the preparation of isolated members of such series, but the authors desire to reserve this field of research.

Complete resolutions have been effected in the case of the following alcohols, the figures being the rotation,  $\alpha_D$ , in a 100 mm. tube at the temperature of the laboratory:—

Methyltert.-butylcarbinol,  $+6.4^\circ$ ;  $\alpha$ -naphthylmethylcarbinol,  $+16.0^\circ$ ; ethylpropylcarbinol,  $+1.5^\circ$ ; ethylisobutylcarbinol,  $+16.3^\circ$ ; propylisobutylcarbinol,  $+2.2^\circ$ ; benzylmethylcarbinol,  $+26.6^\circ$ ; phenylethylmethylcarbinol,  $+14.0^\circ$ . Further experiments have shown that the resolution of the following can also be readily carried out:—Cinnamylmethylcarbinol, cyclohexylmethylcarbinol, isopropylisobutylcarbinol, and phenyl-o-tolylcarbinol.

It is further proposed to include in the scope of the investigations such acids as have analogous constitutions to the optically active alcohols obtained. In some preliminary experiments carried out in conjunction with G. T. Byrne, the following optically active acids have been obtained:— $\alpha$ -Phenylpropionic acid,  $[\alpha]_D^{20} +91.8^\circ$ ; and  $\alpha$ -phenylbutyric acid,  $[\alpha]_D^{20} +84.8^\circ$ .

36. "The Methyl, Ethyl, and isoButyl Esters of Di-trichloroacetyl tartaric Acid, and the Existence of Minima in their Temperature-rotation Curves." By THOMAS STEWART PATTERSON and ALFRED DAVIDSON.

The preparation of the methyl, ethyl, and isobutyl esters of di-trichloroacetyl tartaric acid was described; the rotation values of these esters were quoted and compared amongst themselves, and with the data for other analogous compounds. The existence of minima in the temperature-rotation curves of the esters was also commented on.

## INSTITUTE OF CHEMISTRY.

THE Thirty-fourth Annual General Meeting of the Institute of Chemistry was held at 30, Bloomsbury Square, on Friday, March 1st, Dr. GEORGE BEILBY, F.R.S., the President, occupying the Chair.

In moving the adoption of the Annual Accounts and the Report of the Auditors, Mr. A. GORDON SALAMON, Hon. Treasurer, indicated that the Council had continued the policy of developing the work of the Institute as much as its resources would allow, to the utmost benefit of the members and students. During the past ten years the membership had increased by 331, and the number of registered students had increased by 204; the latter figure indicating that there was good reason to hope that the advance in the membership would be continued. The Building Fund had made good progress, but he hoped that the Council would yet receive a response from Fellows and Associates who had not contributed.

Mr. WALTER F. REID seconded, and a hearty vote of thanks was accorded to the Auditors.

Sir WILLIAM TILDEN moved the reception of the Report of Council for 1911-1912, remarking on the increase in recognition of the Institute and its work, and the professional status of its members during the past twenty years. He paid a high tribute to the work of Dr. Beilby as President during the past three years.

Mr. A. CHASTON CHAPMAN seconded, and after some comments by Col. CHARLES E. CASSAL on the action taken by the Institute on behalf of the professional interests of its members, the Report was duly received and adopted.

Dr. GEORGE BEILBY, F.R.S., the retiring President, then delivered his Address. He showed that during his period of office (1909-12) the Institute had increased by 102 members and 86 students, while the number of candidates for examination during the same period had increased by about 20. The scheme for raising a fund for new buildings for the Institute had made substantial progress, and had reached the sum of over £8500 of the £15,000 considered necessary for the erection of a simple but dignified building suitable for carrying on the work of the Institute. Speaking of the prospects of the profession of chemistry, he believed that there was plenty of room for men of the right stamp, both in educational and industrial work. The Institute had been able to secure appointments for many young members of the profession, and, indeed, lately it had been difficult to find candidates for appointments offering quite good commencing salaries and fair prospects. Touching on the difficulties which confront public analysts and private practitioners, he referred to the attempts made on the part of certain local authorities to lower the status of the professional chemist by offering appointments at ridiculous remuneration. The Institute had decided to take a new and somewhat drastic step by issuing a notice to Fellows and Associates advising them not to apply for appointments advertised by the Metropolitan Boroughs of Lambeth and Wandsworth, both of which at the present time seek to appoint a public analyst, who will be required to provide a laboratory, duly equipped, and a deputy, and to examine possibly as many as two thousand samples, for £500 per annum; while the County of Antrim seek to appoint a public analyst to examine an indefinite number of samples, almost certainly

over eight hundred a year, at a salary of £150. The more enlightened municipal bodies realise that the proper administration of important statutes, such as the Sale of Food and Drugs Act, cannot be expected unless they succeed in attracting to their appointments men of competence and integrity, and, moreover, men who can hold their own as responsible representative officers of their authorities. The Act is as much a statute against fraud as in the interests of public health, and it must be clearly understood that the public analyst is in no way subject to the control of the medical officer of health. It was a false notion that medical men were capable of controlling chemical laboratories. Very few of them possessed anything approaching a competent knowledge of chemistry in any one of its branches, and it was astonishing to find Government authorities in some of our overseas dominions requiring doctors of medicine to supervise qualified professional chemists engaged in laboratories mainly devoted to the analysis of metals and ores. Dr. Beilby referred to important changes which were being made in educational appointments, particularly the Chairs of Chemistry at the Royal College of Science, Dublin, Oxford University, and University College, London, indicating how men who had achieved great things were making way for the younger generation of chemists, to whom we look to maintain the honour of the British School of Chemistry, to which their predecessors had contributed so much. During the past year the Council had inaugurated a new scheme of lectures, mainly intended to help registered students and the younger members, such lectures being given by acknowledged experts in various branches, and illustrating the actual work of practice as distinct from purely academic training.

A vote of thanks to the President for his Address was moved by Mr. DAVID HOWARD, and seconded by Mr. R. FORBES CARPENTER.

Dr. L. T. Thorne, Mr. L. Myddelton Nash, and Mr. W. J. Atkinson Butterfield were appointed Honorary Auditors for the ensuing year.

A ballot having been taken, Dr. George Beilby, F.R.S.; Prof. Percy F. Frankland, F.R.S.; Mr. David Howard; and Sir William Tilden, F.R.S., were declared elected as Censors.

The President and Council for the ensuing year were declared elected.

*President*—Raphael Meldola, D.Sc., LL.D., F.R.S.

*Vice-Presidents*—G. T. Beilby, LL.D., F.R.S.; Frank Clowes, D.Sc.; George McGowan, Ph.D.; Sir Alexander Pedler, C.I.E., F.R.S.; J. Millar Thomson, LL.D., F.R.S.; Sir William A. Tilden, D.Sc., LL.D., F.R.S.

*Hon. Treasurer*—A. Gordon Salamon, A.R.S.M.

*Members of Council*—F. W. F. Arnaud; E. J. Bevan; Bertram Blount; A. G. Bloxam; James Connah, B.Sc.; W. S. Curphey; Cyril Dickinson; J. J. Dobbie, Ph.D., LL.D., F.R.S.; W. P. Dreaper; M. O. Forster, D.Sc., F.R.S.; J. A. Foster; Sir Richard Garton; F. W. Harbord, A.R.S.M.; Otto Hehner; G. W. Monier-Williams, B.A., Ph.D.; W. H. Perkin, LL.D., Ph.D., F.R.S.; T. S. Price, D.Sc., Ph.D.; Charles Proctor; Sir Boverton Redwood, Bart., D.Sc.; H. Droop Richmond; C. A. Seyler, B.Sc.; Alfred Smetham; Thomas Stenhouse, jun., B.Sc., A.R.S.M.; Oliver Trigger; E. W. Voelcker, A.R.S.M.; John White; Sydney Young, D.Sc., F.R.S.

Royal Institution.—On Tuesday next, March 12th, at 3 o'clock, Dr. T. Rice Holmes begins a course of three lectures at the Royal Institution on "Ancient Britain"; and on Thursday afternoon, March 21st, Dr. F. A. Dixey delivers the first of two lectures on "Dimorphism in Butterflies." The Friday Evening Discourse on March 15th will be delivered by Frederick Soddy on "The Origin of Radium"; on March 22nd, by Prof. d'Arcy W. Thompson, on "The North Sea and its Fisheries"; and on March 29th, by Prof. Sir J. J. Thomson, on "Results of the Application of Positive Rays to the Study of Chemical Problems."

## NOTICES OF BOOKS.

*A Brief Laboratory Guide for Qualitative Analysis.* By ARTHUR E. HILL, Ph.D. Easton, Pa.: The Chemical Publishing Co. London: Williams and Norgate. 1911.

THIS book was written for a brief introductory course of inorganic qualitative analysis for the use of the civil engineering students at New York University. The special difficulty which the author, who is the Assistant Professor of Analytical Chemistry at the University, had to face was the exceedingly short time allotted to his subject. This time amounted to only six hours weekly for one half year, and it was found that an adapted course made by curtailing and selecting from any well-known text-book did not give good results, the students' knowledge being too extended from some points of view and too incomplete from others. To meet the case the author devised the scheme he describes in this book, and in the special circumstances it would probably be found satisfactory. Obviously a good deal of the usual course of qualitative analysis would have to be omitted if the work were to be performed in less than 100 hours, and on the whole the author has exhibited good judgment in making the omissions, which are limited to the methods of detecting such commercially unimportant metals as cadmium and strontium, and to the consideration of the complications which result from, for example, the simultaneous presence of phosphates and the alkaline earth metals. The experimental directions are clear, and in every case some indication is given of suitable quantities of substance to employ and of the strengths of the solutions to be used. A useful summary at the end of the book will be found a great help in revision, but the student would undoubtedly find the book more convenient if there were some tables or tabular schemes in it.

*The Technical Analysis of Brass and the Non-ferrous Alloys.* By WILLIAM BENHAM PRICE and RICHARD K. MEADE. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1911.

THIS book will be found useful as an introductory laboratory guide for students in technical schools and colleges. It gives practical instructions for the analysis of many non-ferrous alloys by gravimetric, volumetric, and electrolytic methods, and a student who has been through a short preliminary course of quantitative work would probably find the directions sufficiently full to enable him to arrive at satisfactory results without any extraneous help. A short chapter on electrochemical analysis explains the apparatus required and the methods employed in the electrolytic determination of the metals. Many examples of alloy analysis are included, with precise working details, and the authors have made the best use of the standard authorities on analysis, while they have also inserted the results of some private communications from chemists of note who have worked out modifications of the processes usually adopted. No micrographical methods of studying alloys are included, but as regards chemical methods and elementary work on alloy analysis the book appears to be satisfactory.

*Subject List of Works on Peat, &c., in the Library of the Patent Office.* Published at the Patent Office. 1911 (6d.).

THIS catalogue issued by the Patent Office Library is one of the new series of subject lists, in which sufficient information is given to enable the locations of the books in the Library to be determined. The arrangement of the lists is excellent, giving the reader every possible assistance in looking up any particular subject or section of a subject. The works in the list include those on Peat, Destructive Distillation, Artificial Lighting, Mineral Oils and Waxes, Gaslighting, and Acetylene.



*Bulletin of the Bureau of Agricultural Intelligence and of Plant Diseases.* No. 6. Rome: Printing Office of the International Institute of Agriculture, 1911.

THIS *Bulletin* is one of the publications of the International Institute of Agriculture, and consists of abstracts from the books, periodicals, and bulletins which reached the library of the Institute at Rome during the month of June, 1911. The abstracts are classified, and have been carefully prepared from the originals. The articles upon which they are based have come from all parts of the world and deal with a great variety of subjects, and it is not surprising that they are of very variable value—some giving accounts of really important researches and observations, while others are of purely local and passing interest. The *Bulletin*, which is issued monthly, is also to be obtained in a French edition.

## CORRESPONDENCE.

### CANADIUM.

To the Editor of the Chemical News.

SIR,—Referring to the letter of Mr. Wm. Hamilton Patterson in your issue of February 16th (CHEMICAL NEWS, cv., 84) concerning the supposed new element "Canadium," may I be allowed to put forward a question:—Is it advisable to publish such unripe researches as that of Mr. A. G. French on "Canadium"? It might be true that he really succeeded in coming across a new metal—I do not wish to deny it—but the whole investigation is done in such an unscientific manner that it does not inspire confidence at all, being as it is conducted on businesslike and commercial lines. From Mr. French's letter to his son (CHEMICAL NEWS, civ., 283) we learn that he first found it in May last, and guarded his secret, even from his son, for half a year; during that time he did not find evidently one simple reaction characteristic for the new metal. We do not know even if its solution in hydrochloric acid or aqua regia is precipitated by sulphuretted hydrogen! In these six months which elapsed since his discovery he has not even made the most important thing for a newly discovered element, viz., he has not determined the atomic weight. A few positive analytical reactions (Mr. French enumerates only negative ones) and a provisory determination of atomic weight would safeguard his priority infinitely better than showing it to his banker (!) and lodging a specimen in the bank. In any case, no man of science would proceed in that way, well knowing that the best method to safeguard his rights would be, first, to establish some positive proofs of existence of a new substance (in the first line the atomic weight, the spectrum, and some reactions); second, to publish a short preliminary notice in any of the numerous scientific papers. As it is, Mr. French is not safeguarded at all, for the scanty information derived from the *Glasgow Herald*, or his letter to Mr. Thomas French, cannot be used to ascertain the identity of "Canadium," or to prove the claims of Mr. French, should somebody else come across the same new element.—I am, &c.,

T. ESTREICHER.

Université de Fribourg (Suisse),  
Laboratoire de Chimie II.,  
February 28, 1912.

**Birkbeck College.**—A very interesting event in the history of this College is shortly to be celebrated, when the Chairman of the Governing Body, Mr. James C. N. White, is to be presented with his portrait to mark the completion of fifty years connection with the College. The portrait is being painted by Mr. Seymour Lucas, R.A., and it will be ready for presentation in the early part of the summer. A large number of past students and members are uniting with the Governors and staff in the gift, and it is desired to enlist others, of whom it is felt there are many, who would wish to join. The Secretary of the College will be glad to send particulars to anyone desiring to take part.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. cliv., No. 3, January 15, 1912.

**Cryoscopy in Sodium Hyposulphite with Five Molecules of Water.**—C. Leenhardt and A. Boutaric.—The authors have determined the molecular lowering of the freezing-point of urea in sodium hyposulphite containing exactly five molecules of water. The mean of four concordant experiments was  $K = 42.6^\circ$ , while van't Hoff's formula gives  $K = 42.8$ .

**Atomic Weight of Nitrogen.**—Eugène Wourcel.—The conversion of nitric oxide into nitrogen peroxide may be employed to determine the atomic weight of nitrogen. A U-tube containing nitrogen peroxide is first weighed, and then NO is introduced into it; a second weighing gives the weight of NO employed. A current of pure dry oxygen is then led into the cooled tube until all the nitrous anhydride is converted into peroxide. The slight excess of oxygen is eliminated by evacuation at  $-182^\circ$ , and a final weighing gives the weight of oxygen used. The mean of five determinations was 14.007.

**Preparation of Magnesium Silicide and its Decomposition with Acids.**—A. Besson.—An intimate mixture of dry quartz powder and dry powdered magnesium is ignited in an iron crucible by means of a little magnesium powder on the surface, to which a match is applied. When the reaction is over a homogeneous mass of magnesium silicide is left in the crucible. When it is treated with HCl a mixture of hydrogen and silicomethane and silicoethane is obtained, the amount of the hydrogen silicides present depending on the pressure and the rate of evolution of the gas.

**Compounds of Chromic Hydrate with Amino-acids Derived from Albumins.**—L. Hugounenq and A. Morel.—Chromium oxide, when freshly prepared, combines with various amino-acids giving red solutions. With glycocoll a red solution is obtained from which a red crystalline substance is deposited. This substance contains one molecule of chromium,  $Cr_2$ , combined with two hydroxyls and four molecules of amino-acid. When the solution from which it is deposited is slowly evaporated, another red compound is obtained, containing six molecules of amino-acid to one molecule of chromium,  $Cr_2$ . These tetra- and hexa-derivatives do not behave like true salts of chromium; strong mineral acids do not separate the metal from them, and alkalis act on them only very slowly. They appear to resemble Gregory and Croft's oxalates of chromium, and their formation can be explained by supposing that chromic hydrate plays the part of a hexatomic alcohol, four hydroxyls of which are more readily etherified than the other two.

**Action of Formic Acid on Triarylcannabinols.**—A. Guyot and A. Kovache.—Formic acid readily reduces triarylcannabinols into triarylmethanes according to the equation  $R_3C-OH + HCO_2H = R_3C-H + CO_2 + H_2O$ . With some cannabinols, e.g., triphenylcannabinol, the yield is practically quantitative, but in other cases the amount of carbon dioxide obtained is decidedly inferior to the theoretical quantity.

*Bulletin de la Société Chimique de France.*  
Vol. xi.—xii., No. 2.

**Gases Dissolved in Solids.**—Marcel Guichard.—Numerous experiments have shown that the quantities of gas which dissolve in solids, and particularly in metals, are very considerable. It is found from experiments with phosphorus, cadmium, zinc, potassium, and lead that it

is relatively easy to deprive certain substances of their gases, while others give them up *in vacuo* only very slowly, even if they are converted into the liquid or gaseous states. Potassium is an example of the latter class.

**Extraction of Gases from Copper by Heat.**—Marcel Guichard.—The total elimination by heat of the gases from copper is difficult to effect. It is always necessary to heat for hours *in vacuo*, and the metal employed must have a very large surface. The extraction of the gases by chemical methods confirms this result.

**Molecular Refractions of Azotic Compounds.**—H. Duval.—For all solvents the observed molecular refractions agree very well with those calculated by Brühl's law. With fused azotic compounds the agreement is also good, but the observed results are always decidedly higher than the calculated values. The influence of the ortho- or meta-position of the substituent group is too slight to enable any conclusions to be drawn as to a difference in the constitution of compounds of the two series.

**Characteristic Derivatives and Condensation of Methyl Methoxybenzoylacetaes.**—A. Wahl and C. Silberzweig.—The authors have prepared a number of derivatives of the methyl methoxybenzoylacetaes by the action upon them of such reagents as hydroxylamine and phenylhydrazine, &c., and have determined their physical constants. The methoxybenzoyl acetic ethers are easily transformed into the corresponding methoxyacetophenones by boiling them with ten times their weight of 20 per cent sulphuric acid for about ten hours. The oil is taken up with ether, the ethereal solution is washed with dilute soda, the ether evaporated, and the residue distilled *in vacuo*,—  

$$\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{CO}-\text{CH}_2-\text{COOCH}_3 + \text{H}_2\text{O} =$$

$$= \text{CO}_2 + \text{CH}_3\text{O} + \text{CH}_3\text{O}-\text{C}_6\text{H}_4-\text{CO}-\text{CH}_3.$$

The yield is 60 per cent of the theoretical quantity.

**Colour Reactions of Amino Substances in presence of Mineral Acids and Potassium Bichromate.**—Henri Agulhon and Pierre Thomas.—The authors have studied the colour reactions with sulphuric bichromate solution and nitric bichromate solution of the principal aromatic and fatty amines and the corresponding amino-acids, pyrrol and pyrrolidine carbonic acid, pyridine, piperidine, certain amines with a phenol function, puric bases, urea, guanidine, and their derivatives. Apparently the oxidisability of amino substances is a function of the number of carbons in the molecule. The presence of the group  $\text{NH}_2-\text{CO}_2\text{H}$  in the molecule seems to make it more stable. If a benzene radical is present an olive-green or brown tint is produced.

**Extraction or Determination of Alkaloids in Syrups.**—E. Kohn-Abrest.—To extract alkaloids from syrupy liquids the liquid is well shaken with absolute alcohol and solid potassium carbonate. The alcohol is decanted off, filtered, and distilled; the small residue is taken up with absolute alcohol, filtered, again evaporated, and the residue is taken up with boiling chloroform. The filtered chloroform solution is then evaporated, the final residue is converted into a salt by solution in HCl; the alkaloid chlorhydrate thus obtained corresponds to all the alkaloid in the sugary liquid.

## MISCELLANEOUS.

**Royal Institution.**—A General Monthly Meeting of the Members of the Royal Institution was held on the 4th instant; the Duke of Northumberland, K.G., President, in the Chair. Mr. D. H. Baird, Miss A. E. A. Baker, Commander Virgoe Buckland, Mr. W. T. Burgess, Mr. A. J. M. Duncan, Mr. H. A. Earle, Miss C. H. Farmer, Mr. P. G. C. Foster, Dr. J. A. Harker, the Hon. Sir C. Montagu Lush, Mrs. Said Ruete, Mr. C. F. Smith, Miss C. M. Stainton, Mr. W. A. Tait, and Mr. B. T. Timotheiff were elected Members. The Chairman reported the decease of the Right Hon. Lord Lister, O.M., M.D.,

F.R.S., and a resolution of condolence with the family was passed. The Special Thanks of the Members were returned to Mr. J. C. Simpson for his present of an original letter from Mr. Riebau, the bookbinder to whom Faraday was apprenticed, giving some account of Faraday's early life.

The Elliott Cresson Gold Medal of the Franklin Institute of the State of Pennsylvania.—At the Stated Meeting of the Committee on Science and the Arts held on Wednesday evening, February 7th, 1912, the Elliott Cresson Medal was awarded to—

ALEXANDER GRAHAM BELL, Sc.D., Ph.D., LL.D., of Washington, D.C., in recognition of the value of his solution of the problem of the electrical transmission of articulate speech.

SAMUEL WESLEY STRATTON, D.Eng., Sc.D., of Washington, D.C., in recognition of his distinguished and directive work in physical science and metrology, and its application in the arts and industries.

ALBERT A. MICHELSON, Sc.D., Ph.D., LL.D., of Chicago, Ill., in recognition of his original and fruitful investigations in the field of physical optics.

ALFRED NOBLE, C.E., LL.D., of New York, in recognition of his distinguished achievements in the field of civil engineering.

ELIHU THOMSON, Sc.D., Ph.D., of Swampscott, Mass., in recognition of his leading and distinguished work in the industrial applications of electricity.

EDWARD WILLIAMS MORLEY, Sc.D., Ph.D., LL.D., of West Hartford, Conn., in recognition of his important contributions to chemical science, and particularly of his accurate determinations of fundamental magnitudes.

JOHANN FRIEDRICH ADOLPH VON BAEYER, Ph.D., F.M.R.S., of Munich, Germany, in recognition of the many important results of his extended research in organic chemistry, and of his discovery of synthetic processes of great industrial value.

SIR WILLIAM CROOKES, O.M., D.Sc., LL.D., F.R.S., of London, England, in recognition of his important discoveries in inorganic and analytical chemistry, and of his pioneer work on the discharge of electricity through gases.

SIR HENRY ENFIELD ROSCOE, Ph.D., LL.D., D.C.L., F.R.S., of London, England, in recognition of his extended and important researches in the domains of inorganic, physical, and industrial chemistry.

## MEETINGS FOR THE WEEK.

MONDAY, 11th.—Royal Society of Arts, 8. (Cantor Lecture). "The Loom and Spindle—Past, Present, and Future," by Luther Hooper.

TUESDAY, 12th.—Royal Institution, 3. "Ancient Britain," by Thomas Rice Holmes, Litt.D.  
 — Society of Dyers and Colourists, 8. "Analysis of Weighted Silk," by F. J. Farrell and J. N. Goldsmith. "Paper Yarn, its Production and Uses," by W. P. Dreaper.

WEDNESDAY, 13th.—Royal Society of Arts, 8. "Greek Sculpture," by Prof. Ernest A. Gardner, M.A.

THURSDAY, 14th.—Royal Institution, 3. "Wellington's Army," by Prof. Charles Oman, M.A., &c.  
 — Royal Society of Arts, 4.30. "The Indian Census of 1911," by E. A. Gait, I.C.S., &c.

— Royal Society. "Effects of Ultra-violet Rays upon the Eye," by Dr. E. K. Martin. "Presence of Radium in some Carcinomatous Tumours," by Dr. W. S. Lazarus-Barlow. "An Improved Method for Opsonic Index Estimations involving the Separation of Red and White Human Blood Corpuscles," by C. Russ. "Electrical Conductivity of Bacteria, and the Rate of Inhibition of Bacteria by Electric Currents," by W. M. Thornton. "Critical Study of Experimental Fever," by E. C. Hort and W. J. Penfold. "Certain Results of Drying Non-sporing Bacteria in a Charcoal Liquid Air Vacuum," by S. G. Shattock and L. S. Dudgeon.

FRIDAY, 15th.—Royal Institution, 9. "The Origin of Radium," by F. Soddy, M.A., F.R.S.

SATURDAY, 16th.—Royal Institution, 3. "Molecular Physics," by Sir J. J. Thomson, F.R.S., &c.



# THE CHEMICAL NEWS.

VOL. CV., No. 2729.

## NEW COMPOUNDS OF SAMARIUM AND NEODYMIUM.

By C. JAMES, F. M. HOBEN, and C. H. ROBINSON.

The following compounds were prepared during a search for salts of the rare earths that might be useful for fractionating:—

**Samarium Ethylsulphonate**,  $(C_2H_5SO_3)_6Sm_2 \cdot 6H_2O$ .—Ethylsulphonic acid was heated nearly to boiling, and small quantities of samarium oxide added until no more oxide would dissolve. Finally, a little more acid was added, the whole boiled for a short time, filtered, and evaporated down on the water-bath. The compound gradually crystallised out upon standing. The crystals were freed from the mother-liquor by suction, and washed with acetone.

This salt formed pale yellow crystals, very soluble in water and alcohol, but insoluble in acetone and ether. Upon heating, this substance charred and gave off a strong garlic odour.

Calculated— $Sm_2O_3$ , 32.78; S, 18.08;  $H_2O$ , 10.16.

Found— $Sm_2O_3$ , 32.70; S, 18.17;  $H_2O$ , 10.14.

Samarium ethylsulphonate lost all its water of crystallisation when heated to  $100^\circ$  for four hours.

**Samarium Methylsulphonate**,  $(CH_3SO_3)_6Sm_2 \cdot 7H_2O$ .—This substance was prepared in a similar manner to the former sulphonate. The solution, after filtering and evaporating, was allowed to stand for a day and a half. The crystals were dried as much as possible by suction, and washed with acetone.

This sulphonate formed pale yellow crystals, very soluble in water and alcohol, only slightly soluble in acetone, and insoluble in ether.

Samarium methylsulphonate lost six molecules of water of crystallisation after heating to  $100^\circ$  for some time.

Calculated— $Sm_2O_3$ , 34.97. Found— $Sm_2O_3$ , 35.15.

**Samarium Propylsulphonate**,  $(C_3H_7SO_3)_6Sm_2 \cdot 9H_2O$ .—Obtained like the ethylsulphonate.

This compound did not crystallise well. It was filtered from mother-liquor by suction, and well washed with ether. The result of this treatment was a powder of small crystals, possessing a yellowish tint, soluble in water, alcohol, and acetone, insoluble in ether.

The propylsulphonate, when heated for a long time at  $100^\circ$ , lost eight molecules of water of crystallisation.

Calculated— $Sm_2O_3$ , 29.04. Found— $Sm_2O_3$ , 29.12.

**Samarium Isobutylsulphonate**,  $(C_4H_9SO_3)_6Sm_2 \cdot 7H_2O$ , was prepared by saturating isobutylsulphonic acid with samarium oxide, care being taken to have the solution acid before filtering and evaporating. The concentrated solution was allowed to stand over sulphuric acid for a few days. The crystals were separated and washed with ether.

Samarium isobutylsulphonate lost five molecules of water when kept at  $100^\circ$  for two days.

Calculated— $Sm_2O_3$ , 27.90. Found— $Sm_2O_3$ , 27.97.

**Samarium Camphorsulphonate**,—

$(C_{10}H_{15}OSO_3)_6Sm_2 \cdot 10H_2O$ .

—This sulphonate was obtained as above. When sufficient of the salt had separated the dish was removed from the desiccator, the crystals separated upon a small Buchner funnel, and washed with ether. The crystals were dissolved in alcohol, and the solution allowed to crystallise, after which it was again well washed with ether.

Samarium camphorsulphonate formed a mass of very small crystals, white with only a faint yellow tint. It was very soluble in water, alcohol, and acetone, but insoluble in ether.

This compound, after heating for some time at  $100^\circ$ , became nearly anhydrous.

Calculated— $Sm_2O_3$ , 18.67. Found— $Sm_2O_3$ , 18.61.

**Samarium Methane-trisulphonate**,—

$[CH(SO_3)_2]_2Sm_2 \cdot 16H_2O$ .

—A slightly acid solution of samarium oxide in methane-trisulphonic acid was evaporated and set aside to crystallise. The samarium compound separated very well after standing for a day. The crystals were drained and well washed with alcohol. They were yellowish, transparent, soluble in water, but insoluble in alcohol, acetone, and ether. This salt is very stable, since it can be heated to high temperatures with fuming nitric acid in sealed tubes without decomposition taking place.

Samarium methane-trisulphonate lost two molecules of water after prolonged heating to  $100^\circ$ .

Calculated— $Sm_2O_3$ , 31.84. Found  $Sm_2O_3$ , 31.88.

**Samarium 1-3-4-Meta-xylenesulphonate**,—

$[C_6H_3(CH_3)_2SO_3]_6Sm_2 \cdot 7H_2O$ .

—A concentrated solution of samarium-oxide in the xylenesulphonic acid crystallised after standing some time. The acid was drained and washed with acetone. It formed small very pale yellow crystals, soluble in water and alcohol, insoluble in acetone and ether.

Calculated— $Sm_2O_3$ , 22.69. Found— $Sm_2O_3$ , 22.65.

**Samarium Glycollate**,  $(CH_2.OH.COO)_6Sm_2$ .—Samarium hydroxide was gradually added to cold glycollic acid. Upon heating the filtered solution the salt separated as a very dense precipitate which was almost insoluble in water.

Samarium glycollate differs from yttrium glycollate, inasmuch as the former is anhydrous while the latter contains two molecules of water of crystallisation (Pratt and James, *Journ. Am. Chem. Soc.*, xxxiii., 1330).

Calculated— $Sm_2O_3$ , 46.44. Found— $Sm_2O_3$ , 46.54.

**Samarium Cacodylate**,  $[(CH_3)_2AsO_2]_6Sm_2 \cdot 16H_2O$ .—This substance was obtained by boiling a solution of cacodylic acid with samarium hydroxide. The last portions of samarium hydroxide were dissolved by the careful addition of more acid. Upon cooling, the solution crystallised. The whole was poured upon a Buchner funnel, and the crystals washed with alcohol and dried.

The cacodylate forms white crystals which are soluble in hot water, insoluble in alcohol and acetone.

When kept at  $100^\circ$  for three hours all water of crystallisation was lost.

Calculated— $Sm_2O_3$ , 24.73;  $H_2O$ , 20.43.

Found— $Sm_2O_3$ , 24.81;  $H_2O$ , 20.43.

**Samarium Ethylene-disulphonate**,—

$[C_2H_4(SO_3)_2]_3Sm_2 \cdot 4H_2O$ ,

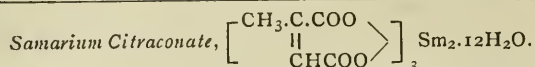
was prepared by saturating ethylene-disulphonic acid with samarium hydroxide. The solution was made slightly acid, filtered, and evaporated. The salt separated well. It formed yellow transparent crystals soluble in water, slightly soluble in alcohol and insoluble in acetone.

Calculated— $Sm_2O_3$ , 37.22. Found— $Sm_2O_3$ , 37.04.

**Samarium Ethylglycollate**,—

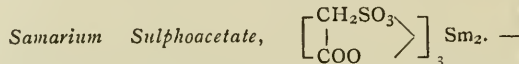
$(C_2H_5O.CH_2COO)_6Sm_2 \cdot 18H_2O$ ?

separated from concentrated solution in large yellow transparent crystals which contained included mother-liquor. An analysis showed the presence of eighteen molecules of water of crystallisation. However, since there was doubt about mother-liquor, the study of the rare earth ethylglycollates will be continued at an early opportunity with large amounts of material.



—Citraconic acid was saturated with samarium hydroxide, filtered, and concentrated. The compound which separated out upon standing was removed by suction, and the mass of citraconate washed with alcohol and acetone.

Calculated— $\text{Sm}_2\text{O}_3$ , 38.72. Found— $\text{Sm}_2\text{O}_3$ , 38.88.



Samarium hydroxide rapidly dissolved in sulphoacetic acid. No crystals were obtained by evaporation and leaving over sulphuric acid. The solution merely formed a thick sticky mass.

*Samarium Hydroxyethanesulphonate.*—A concentrated solution of this compound would not crystallise when allowed to remain in a desiccator over sulphuric acid.

*Neodymium Methylsulphonate*,  $(\text{CH}_3\text{SO}_3)_6\text{Nd}_2 \cdot 7\text{H}_2\text{O}$ .—Methylsulphonic acid was saturated with neodymium oxide and filtered. The concentrated solution solidified to a crystalline mass, when left in a desiccator over sulphuric acid. The crystals were broken up and well washed with ether. They were very soluble in water, soluble in alcohol, and slightly so in acetone, but insoluble in ether. It lost six molecules of water of crystallisation at  $100^\circ$  similarly to the samarium compound.

Calculated— $\text{Nd}_2\text{O}_3$ , 34.17. Found— $\text{Nd}_2\text{O}_3$ , 34.24.

*Neodymium Ethylsulphonate*,  $(\text{C}_2\text{H}_5\text{SO}_3)_6\text{Nd}_2 \cdot 6\text{H}_2\text{O}$ .—The formation of this compound was brought about in the same manner as the preceding. It appeared to be less soluble than the methylsulphonate, however, for it crystallised easily upon evaporation and being allowed to stand for a short time. The powdered salt was washed with ether. It possessed a pale amethyst colour, was insoluble in acetone and ether, soluble in alcohol, and very soluble in water.

Calculated— $\text{Nd}_2\text{O}_3$ , 32.02;  $\text{H}_2\text{O}$ , 10.28.

Found— $\text{Nd}_2\text{O}_3$ , 32.05;  $\text{H}_2\text{O}$ , 9.97.

*Neodymium Propylsulphonate*,  $\text{C}_3\text{H}_7\text{SO}_3)_6\text{Nd}_2 \cdot 6\text{H}_2\text{O}$ .—A solution of this substance gave upon evaporation a voluminous mass of small crystals. They were washed with ether and dried. The propylsulphonate is very soluble in water, soluble in acetone and alcohol. After heating for some time to  $100^\circ$  one molecule of water remains.

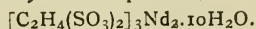
Calculated— $\text{Nd}_2\text{O}_3$ , 29.65. Found— $\text{Nd}_2\text{O}_3$ , 29.63.

*Neodymium Isobutylsulphonate*,  $\text{C}_4\text{H}_9\text{SO}_3)_6\text{Nd}_2$ .—Crystals of this compound formed with difficulty. They were voluminous, pale amethyst, soluble in alcohol and very soluble in water.

The estimation of  $\text{Nd}_2\text{O}_3$  gave results corresponding to  $8\text{H}_2\text{O}$ , this being one molecule more than the samarium compound possessed. Moisture or efflorescence might be the cause of this difference. However, the salts did not seem to be of sufficient importance to make it worth while preparing again.

Calculated— $\text{Nd}_2\text{O}_3$ , 26.81. Found— $\text{Nd}_2\text{O}_3$ , 26.94.

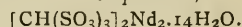
*Neodymium Ethylene-disulphonate*,—



—The acid was carefully neutralised with neodymium oxide. The clear solution was evaporated, after which large amethyst crystals formed. They were insoluble in alcohol and acetone, but very soluble in water. When heated to  $100^\circ$  for a long time the salt gradually lost water until a hydrate containing four molecules of water remained.

Calculated— $\text{Nd}_2\text{O}_3$ , 32.59. Found— $\text{Nd}_2\text{O}_3$ , 32.58.

*Neodymium Methine-trisulphonate*,—

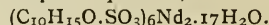


—Fairly large crystals of this substance were obtained by evaporating a solution of the oxide in the corresponding acid. They were of a pale amethyst colour, insoluble in alcohol, acetone, and acetic acid, but very soluble in water. Like most of the other aliphatic sulphonates there was very little difference between the solubilities at room temperature and  $100^\circ$ . This renders these compounds unsuitable for rapid fractionation.

The neodymium trisulphonate, similar to other salts of this acid, is very stable; it is not decomposed by fuming nitric acid under pressure until a high temperature is reached.

Calculated— $\text{Nd}_2\text{O}_3$ , 32.15. Found— $\text{Nd}_2\text{O}_3$ , 32.04.

*Neodymium Camphorsulphonate*,—

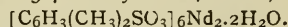


—A solution of this salt, obtained in the usual way, crystallised with difficulty, yielding a fluffy very pale amethyst powder, soluble in alcohol and acetone, and very soluble in water.

Calculated— $\text{Nd}_2\text{O}_3$ , 16.98. Found— $\text{Nd}_2\text{O}_3$ , 17.02.

Several hydrates of the camphorsulphonates appear to exist.

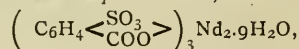
*Neodymium 1.3.4-Metaxylenesulphonate*,—



—This sulphonate separated out during the evaporation on a water-bath in crystalline form. It was of a very pale amethyst colour, insoluble in acetone, slightly soluble in alcohol, and soluble in water.

Calculated— $\text{Nd}_2\text{O}_3$ , 22.46. Found— $\text{Nd}_2\text{O}_3$ , 22.35.

*Neodymium Metasulphobenzozate*,—



formed pale coloured crystals, soluble in alcohol and acetone, and very soluble in water.

Calculated— $\text{Nd}_2\text{O}_3$ , 32.03. Found— $\text{Nd}_2\text{O}_3$ , 32.19.

*Neodymium Quinate*,  $[\text{C}_6\text{H}_7(\text{OH})_4\text{COO}]_6\text{Nd}_2 \cdot 11\text{H}_2\text{O}$ .—Neodymium hydroxide was boiled with quinic acid, the solution filtered and evaporated. The quinate crystallised out upon cooling. Pale amethyst coloured powder, slightly soluble in cold water.

Calculated— $\text{Nd}_2\text{O}_3$ , 20.62. Found— $\text{Nd}_2\text{O}_3$ , 20.61.

*Neodymium Anisate*,  $(\text{C}_6\text{H}_4 \cdot \text{CH}_3 \cdot \text{O} \cdot \text{COO})_6\text{Nd}_2$ .—This compound was precipitated when a slightly acid solution of sodium anisate was added to a nearly neutral solution of neodymium chloride. Free anisic acid was removed from the precipitate by means of hot acetone. The pale coloured precipitate was insoluble in water.

Calculated— $\text{Nd}_2\text{O}_3$ , 28.16; H, 3.54; C, 48.19.

Found— $\text{Nd}_2\text{O}_3$ , 28.17; H, 3.31; C, 48.29.

*Neodymium Oxanilate*,  $(\text{C}_6\text{H}_5\text{NHOCOO})_6\text{Nd}_2 \cdot 5\text{H}_2\text{O}$ .—When neodymium chloride was added to a hot slightly acid solution of sodium oxanilate, a thick sticky mass separated, which rapidly became hard and crystalline upon cooling. The compound was insoluble.

Calculated— $\text{Nd}_2\text{O}_3$ , 24.70. Found— $\text{Nd}_2\text{O}_3$ , 24.69.

*Neodymium Cacodylate*,  $[(\text{CH}_3)_2\text{AsO}_2]_6\text{Nd}_2$ .—Cacodylic acid was saturated with neodymium hydroxide. The liquid was filtered and evaporated. Upon cooling, the salt separated in very soft asbestos like crystals. It was insoluble in alcohol and acetone, slightly soluble in cold water, and soluble in hot water.

Calculated— $\text{Nd}_2\text{O}_3$ , 30.31. Found— $\text{Nd}_2\text{O}_3$ , 30.40.

*Neodymium Hydroxyethanesulphonate*.—A solution containing this compound would not crystallise so as to be workable.

Durham, New Hampshire,  
January 4, 1912.



THE SEPARATION AND ESTIMATION OF  
BARIUM ASSOCIATED WITH CALCIUM AND  
MAGNESIUM, BY THE ACTION OF  
ACETYL CHLORIDE IN ACETONE UPON THE  
MIXED CHLORIDES.

By F. A. GOOCH and C. N. BOYNTON.

IN former papers from the Kent Chemical Laboratory of Yale University (Mar. *Am. Journ. Sci.*, [3], xliii., 521; Havens, *Ibid.*, [4], ii., 416; iv., 111; vi., 45; vi., 396) it has been shown that certain chlorides may be quantitatively precipitated for purposes of analysis by treating their water solutions with aqueous or gaseous hydrochloric acid and ether.

The present paper is an account of procedure for the precipitation of barium chloride from water solution and its separation from calcium and magnesium by the use of acetyl chloride to decompose the water of the solution according to the reaction  $\text{CH}_3\text{COCl} + \text{H}_2\text{O} = \text{CH}_3\text{COOH} + \text{HCl}$ , inconvenient violence of reaction being moderated by the addition of acetone, which mixes in all proportions with both acetyl chloride and water and by itself exerts no appreciable solvent action upon barium chloride.

When a mixture of acetone and acetyl chloride, preferably 4 : 1, is added slowly to a very concentrated solution of barium chloride in water, the water is attacked at once, hydrogen chloride is liberated, and precipitation begins immediately. If the temperature is kept down during the process by immersing in cool running water the vessel in which reaction takes place, no more than a mere trace of barium can be detected by sulphuric acid in the residue left after evaporating the liquid separated from the precipitate by filtration through asbestos. When, however, the temperature is allowed to rise, in consequence of the heat liberated in the reaction, an appreciable amount of barium may be found by sulphuric acid in the filtrate. In Table I. are given the data of experiments in which the residue obtained (a) by treating a solution of barium chloride in 1 cc. of water with 30 cc. of a 4 : 1 acetone-acetyl chloride mixture and collecting the precipitate upon asbestos in a perforated crucible, washing with acetone and with ether, was weighed after drying in air, then (b) treated on the asbestos for ten minutes with 15–20 cc. of acetyl chloride, washed with acetone and with ether, dried in the air and weighed, then (c) digested for ten minutes with 20–25 cc. of 2 : 1 acetone-acetyl chloride mixture, washed with acetone and with ether, dried in the air and weighed, and then (d) heated in the air-bath, or to low redness, and weighed.

From these results it appears (a) that when the acetone-acetyl chloride mixture (4 : 1) acts upon the cooled concentrated water solution of barium chloride the precipitate is the hydrous chloride,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ , only the water in excess of that needed to form the hydrous salt being immediately attacked; (b) that acetyl chloride by itself produces only slight dehydration of the salt without marked solubility; and (c) that prolonged action of the acetone-acetyl chloride mixture (2 : 1) results in appreciable dehydration and considerably increased solubility of the salt. By further experimentation it was shown that when the acetone-acetyl chloride mixture is added without cooling to the water solution of barium chloride, the heat of reaction favours dehydration of the hydrous salt, and the anhydrous salt may go into solution to the amount of several mgrms. in 10 cc. of the precipitating mixture. Upon filtering the mixture and treating the filtrate with acetone, with acetyl chloride, or with the acetone-acetyl chloride mixture, the dissolved anhydrous salt is not thrown out of solution, but the addition of a drop of water is sufficient to induce immediate precipitation in the form of the hydrous salt.

Incidentally it is interesting to note that when water acts upon the colourless mixture of acetone and acetyl chloride the solution becomes yellow, and then reddish,

and develops a distinctly fruity odour, condensation taking place between the acetone and acetyl chloride. The boiling-points of the collected filtrates from a series of barium chloride precipitations after standing about a week ranged from 50.5° to 250°, and left a resinous residue at that temperature.

From the results of the experiments described, it may be inferred that the best conditions for the quantitative precipitation of barium chloride by the acetone-acetyl chloride mixture should be found in the use of minimum amounts of water, the preservation of ordinarily low temperature, a liberal proportion of acetone, and not too prolonged digestion of the precipitate in the excess of the precipitant. These conditions have been complied with in the quantitative tests.

Barium chloride was prepared for the work by precipitating it with strong hydrochloric acid from a water solution of the presumably pure salt, re-crystallising twice from water, and drying in the air. On gentle ignition the salt lost water corresponding to the ideal composition of the hydrous chloride,  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ . In each test a portion of this salt was weighed out into a small beaker and dissolved in 1 cc. of water. The beaker was cooled by immersion in a water-bath preferably supplied with running water at a temperature of about 15°. To the cooled solution, constantly shaken, the acetone-acetyl chloride mixture was added from a dropping funnel at the rate of five drops to the second. Other data of the experiments with barium chloride are given in Table II. The precipitate was filtered off upon asbestos in a perforated crucible, dried, or ignited, and weighed as the anhydrous chloride,  $\text{BaCl}_2$ . From these results it appears that the best of the conditions studied for the handling of 0.1 gm. of hydrous barium chloride are the solution of the salt in 1 cc. of water, treatment with 30 cc. of the 4 : 1 mixture of acetone and acetyl chloride, washing with acetone, and drying in the air-bath at 135° or at low redness.

The application of these conditions to the separation of barium from moderate amounts of calcium and magnesium proves to be easily feasible. When acetone is added to the concentrated solution of calcium chloride or magnesium chloride in water two liquid layers are formed, the acetone above and the aqueous layer below; but the addition of a few drops of acetyl chloride renders the liquids miscible while further addition causes no precipitation. When the 4 : 1 mixture of acetone and acetyl chloride is added at the rate of five drops in the second to the solution containing no more than 0.5 gm. of the calcium and magnesium salts, barium chloride is precipitated and calcium chloride and magnesium chloride are dissolved; but when the soluble chloride is present in the proportion of 1.0 gm. to 0.1 gm. of the barium chloride, the rate of addition of the precipitating mixture should not be greater than two drops in the second at the start in order to avoid inclusion of the soluble salt in the insoluble barium salt. Even in such cases the mixture may be added at the rate of five drops in the second, after the greater part of the barium is down. Tables III. and IV. contain the data of experiments upon the separation of barium from calcium and magnesium. The results obtained in the separation of 0.1 gm. of the barium salt from 0.5 gm. of calcium and magnesium salts are excellent.

The separation of barium from strontium proves not to be so simple. When the 4 : 1 mixture of acetone and acetyl chloride is added to the concentrated water solution of 0.1 gm. of strontium chloride a partial precipitation takes place. When the precipitate thus produced was filtered off, washed with acetone and with ether, and dried in air, it lost water amounting to 19.93 per cent and 20.00 per cent of its weight on heating to 135°. Obviously the salt was essentially  $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$ , which should contain theoretically 18.51 per cent of water. This precipitate of  $\text{SrCl}_2 \cdot 2\text{H}_2\text{O}$  when treated with a mixture of acetone and acetyl chloride containing a larger proportion of the latter, goes into solution and is again partially precipitated upon increasing the proportion of acetone, essentially as

TABLE I.

|                                                                                                                                                                | Experiment I.   |               | Experiment II.  |               |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------|---------------|-----------------|---------------|
|                                                                                                                                                                | Weight (gram.). | Loss (gram.). | Weight (gram.). | Loss (gram.). |
| BaCl <sub>2</sub> ·2H <sub>2</sub> O taken .. .. .                                                                                                             | 0.1012          | —             | 0.1000          | —             |
| (a). Residue after precipitation, washing, and drying in air ..                                                                                                | 0.1008          | 0.0004        | 0.0996          | 0.0004        |
| (b). Residue after treatment with acetyl chloride, washing, and drying in air .. .. .                                                                          | 0.1006          | 0.0002        | 0.0996          | 0.0000        |
| (c). Residue after treatment with acetone-acetyl chloride mixture, washing, and drying in air .. .. .                                                          | 0.0985          | 0.0021        | 0.0981          | 0.0015        |
| (d). Residue after heating, BaCl <sub>2</sub> .. .. .                                                                                                          | 0.0846*         | —             | 0.0839†         | —             |
| BaCl <sub>2</sub> ·2H <sub>2</sub> O corresponding to BaCl <sub>2</sub> found .. .. .                                                                          | 0.0993          | —             | 0.0985          | —             |
| Loss of BaCl <sub>2</sub> ·2H <sub>2</sub> O due to solubility and dehydration ..                                                                              | —               | 0.0027        | —               | 0.0019        |
| Loss of BaCl <sub>2</sub> ·2H <sub>2</sub> O due to solubility, calculated from BaCl <sub>2</sub> ·2H <sub>2</sub> O taken and BaCl <sub>2</sub> found .. .. . | —               | 0.0019        | —               | 0.0015        |
| Loss by dehydration .. .. .                                                                                                                                    | —               | 0.0008        | —               | 0.0004        |

TABLE II.—The Estimation of Barium.

|     | BaCl <sub>2</sub> taken as BaCl <sub>2</sub> ·2H <sub>2</sub> O. | BaCl <sub>2</sub> found. | Error.   | Water to dissolve BaCl <sub>2</sub> ·2H <sub>2</sub> O. | Amount of mixture and composition by volume |              |
|-----|------------------------------------------------------------------|--------------------------|----------|---------------------------------------------------------|---------------------------------------------|--------------|
|     | Grm.                                                             | Grm.                     | Grm.     | Cc.                                                     | To precipitate.                             | To wash.     |
| 1.  | 0.0859                                                           | 0.0859                   | 0.0000†  | I                                                       | 5 cc. 2 : I                                 | 10 cc. 2 : I |
| 2.  | 0.0861                                                           | 0.0854                   | -0.0007† | I                                                       | 5 " 2 : I                                   | 10 " 2 : I   |
| 3.  | 0.0861                                                           | 0.0858                   | -0.0003† | I                                                       | 5 " 2 : I                                   | 10 " 2 : I   |
| 4.  | 0.0862                                                           | 0.0854                   | -0.0008* | I                                                       | 6 " 2 : I                                   | 10 " 2 : I   |
| 5.  | 0.0857                                                           | 0.0854                   | -0.0003* | I                                                       | 6 " 2 : I                                   | 10 " 2 : I   |
| 6.  | 0.0858                                                           | 0.0860                   | +0.0002* | I                                                       | 6 " 2 : I                                   | 30 " 4 : I   |
| 7.  | 0.0860                                                           | 0.0859                   | -0.0001* | I                                                       | 6 " 2 : I                                   | 30 " 4 : I   |
| 8.  | 0.0853                                                           | 0.0850                   | -0.0003* | I                                                       | 6 " 2 : I                                   | Acetone.     |
| 9.  | 0.0854                                                           | 0.0848                   | -0.0006* | I                                                       | 6 " 2 : I                                   | "            |
| 10. | 0.0852                                                           | 0.0851                   | -0.0001* | I                                                       | 6 " 2 : I                                   | "            |
| 11. | 0.0857                                                           | 0.0856                   | -0.0001† | I                                                       | 6 " 2 : I                                   | "            |
| 12. | 0.0852                                                           | 0.0845                   | -0.0007† | I                                                       | 6 " 2 : I                                   | "            |
| 13. | 0.0855                                                           | 0.0852                   | -0.0003† | I                                                       | 6 " 2 : I                                   | "            |
| 14. | 0.0862                                                           | 0.0862                   | 0.0000†  | I                                                       | 30 " 4 : I                                  | "            |
| 15. | 0.0868                                                           | 0.0868                   | 0.0000†  | I                                                       | 30 " 4 : I                                  | "            |

TABLE III.—The Separation of Barium from Calcium.

|     | BaCl <sub>2</sub> taken as BaCl <sub>2</sub> ·2H <sub>2</sub> O. | CaCl <sub>2</sub> ·2H <sub>2</sub> O taken. | BaCl <sub>2</sub> found. | Error.   | Water used to dissolve salts. | Amount of mixture (4 : 1) used. |
|-----|------------------------------------------------------------------|---------------------------------------------|--------------------------|----------|-------------------------------|---------------------------------|
|     | Grm.                                                             | Grm.                                        | Grm.                     | Grm.     | Cc.                           | Cc.                             |
| 1.  | 0.0859                                                           | 0.1000                                      | 0.0859                   | 0.0000†  | I                             | 30                              |
| 2.  | 0.0867                                                           | 0.1040                                      | 0.0867                   | 0.0000†  | I                             | 30                              |
| 3.  | 0.0868                                                           | 0.1022                                      | 0.0868                   | 0.0000†  | I                             | 30                              |
| 4.  | 0.0865                                                           | 0.1020                                      | 0.0865                   | 0.0000†  | I                             | 30                              |
| 5.  | 0.0868                                                           | 0.1017                                      | 0.0869                   | +0.0001† | I                             | 30                              |
| 6.  | 0.0864                                                           | 0.1016                                      | 0.0861                   | -0.0003† | I                             | 30                              |
| 7.  | 0.0866                                                           | 0.3025                                      | 0.0867                   | +0.0001† | 1½                            | 30                              |
| 8.  | 0.0859                                                           | 0.5025                                      | 0.0859                   | 0.0000†  | 2                             | 30                              |
| 9.  | 0.0860                                                           | 1.0020                                      | 0.0878                   | +0.0018† | 3                             | 30                              |
| 10. | 0.0859                                                           | 1.0020                                      | 0.0855                   | -0.0004§ | 2                             | 30                              |
| 11. | 0.0864                                                           | 1.0035                                      | 0.0867                   | +0.0003§ | 2                             | 30                              |

TABLE IV.—The Separation of Barium from Magnesium.

|     | BaCl <sub>2</sub> taken as BaCl <sub>2</sub> ·2H <sub>2</sub> O. | MgCl <sub>2</sub> ·6H <sub>2</sub> O taken. | BaCl <sub>2</sub> found. | Error.   | Water used to dissolve salt. | Amount of mixture (4 : 1) used. |
|-----|------------------------------------------------------------------|---------------------------------------------|--------------------------|----------|------------------------------|---------------------------------|
|     | Grm.                                                             | Grm.                                        | Grm.                     | Grm.     | Cc.                          | Cc.                             |
| 1.  | 0.0858                                                           | 0.1000                                      | 0.0857                   | -0.0001† | I                            | 30                              |
| 2.  | 0.0869                                                           | 0.1025                                      | 0.0870                   | +0.0001† | I                            | 30                              |
| 3.  | 0.0858                                                           | 0.1025                                      | 0.0858                   | 0.0000†  | I                            | 30                              |
| 4.  | 0.0862                                                           | 0.1010                                      | 0.0863                   | +0.0001† | I                            | 30                              |
| 5.  | 0.0858                                                           | 0.1006                                      | 0.0860                   | +0.0002† | I                            | 30                              |
| 6.  | 0.0860                                                           | 0.1020                                      | 0.0859                   | -0.0001† | I                            | 30                              |
| 7.  | 0.0860                                                           | 0.1010                                      | 0.0862                   | +0.0002† | I                            | 30                              |
| 8.  | 0.0865                                                           | 0.3010                                      | 0.0867                   | +0.0002† | 1½                           | 30                              |
| 9.  | 0.0864                                                           | 0.5000                                      | 0.0867                   | +0.0003† | 2                            | 30                              |
| 10. | 0.0868                                                           | 1.0015                                      | 0.0878                   | +0.0010† | 3                            | 30                              |
| 11. | 0.0853                                                           | 1.0010                                      | 0.0854                   | +0.0001§ | 3                            | 30                              |

\* Heated to low redness.

† Heated to 135° for one and a-half hours.

‡ The precipitant was added at first at the rate of five drops in the second.

§ The precipitant was added at the rate of two drops in the second at the outset, and later of five drops in the second



TABLE V.—The Separation of Barium from Strontium.

|     | BaCl <sub>2</sub> taken as<br>BaCl <sub>2</sub> ·2H <sub>2</sub> O. | SrCl <sub>2</sub> taken. | BaCl <sub>2</sub> found. | Error.  | Water used<br>to dissolve salt. | Amount of mixture<br>(2 : 1) used. |
|-----|---------------------------------------------------------------------|--------------------------|--------------------------|---------|---------------------------------|------------------------------------|
|     | Grm.                                                                | Grm.                     | Grm.                     | Grm.    | Cc.                             | Cc.                                |
| 1.  | 0.0867                                                              | 0.0385                   | 0.0923                   | +0.0056 | 1                               | 30                                 |
| 2.  | 0.0866                                                              | 0.0304                   | 0.0857                   | -0.0009 | 1                               | 30                                 |
| 3.  | 0.0860                                                              | 0.0320                   | 0.0861                   | +0.0001 | 1                               | 30                                 |
| 4.  | 0.0856                                                              | 0.0315                   | 0.0840                   | -0.0016 | 1                               | 30                                 |
| 5.  | 0.0856                                                              | 0.0307                   | 0.0848                   | -0.0008 | 1                               | 30                                 |
| 6.  | 0.0859                                                              | 0.0304                   | 0.0839                   | -0.0020 | 1                               | 30                                 |
| 7.  | 0.0862                                                              | 0.0307                   | 0.0859                   | -0.0003 | 1                               | 30                                 |
| 8.  | 0.0857                                                              | 0.0315                   | 0.1160                   | +0.0303 | 0.5                             | 30                                 |
| 9.  | 0.0857                                                              | 0.0317                   | 0.1058                   | +0.0201 | 0.5                             | 30                                 |
| 10. | 0.0853                                                              | 0.0315                   | 0.1083                   | +0.0230 | 0.5                             | 30                                 |
| 11. | 0.0869                                                              | 0.0305                   | 0.1043                   | +0.0174 | 0.5                             | 30                                 |
| 12. | 0.0863                                                              | 0.0307                   | 0.0906                   | +0.0043 | 0.5                             | 30                                 |
| 13. | 0.0859                                                              | 0.0308                   | 0.0849                   | -0.0010 | 0.5                             | 30                                 |
| 14. | 0.0869                                                              | 0.0108                   | 0.0870                   | +0.0001 | 1                               | 30                                 |
| 15. | 0.0865                                                              | 0.0110                   | 0.0858                   | -0.0007 | 1                               | 30                                 |
| 16. | 0.0853                                                              | 0.0115                   | 0.0853                   | —       | 1                               | 30                                 |
| 17. | 0.0861                                                              | 0.0109                   | 0.0870                   | +0.0009 | 1                               | 30                                 |

SrCl<sub>2</sub>·2H<sub>2</sub>O. When a mixture richer in acetyl chloride, the 2 : 1 mixture of acetone-acetyl chloride, is added to the concentrated water solution of strontium chloride, the precipitate first formed is slowly re-dissolved in a sufficient excess of the mixture and again partially precipitated upon the addition of more acetone. This second precipitate of SrCl<sub>2</sub>·2H<sub>2</sub>O is not completely soluble, however, when the proportion of acetyl chloride is again increased, but will dissolve upon the addition of an acetone-acetyl chloride mixture to which a few drops of water have been previously added, and which is, therefore, charged with hydrogen chloride. So it appears that the solubility of the strontium chloride, SrCl<sub>2</sub>·2H<sub>2</sub>O, depends to a very large extent upon the concentration of hydrogen chloride in the mixture.

In attempting the separation of barium from strontium, therefore, it was the 2 : 1 mixture of acetone with acetyl chloride which, on account of its higher power as a solvent for SrCl<sub>2</sub>·2H<sub>2</sub>O, was added to the concentrated water solution of the barium chloride and strontium chloride, though this mixture has been shown to be somewhat less favourable to the complete precipitation of barium chloride than the (4 : 1) mixture containing the larger proportion of acetone, and the addition was made at the rate not greater than two drops in the second, or 30 cc. in ten minutes. The precipitate, filtered upon asbestos and washed with acetone, was dried at 135°. The data of these experiments are recorded in Table V.

The separation of barium from strontium by the process described is obviously only approximate, some barium chloride going into solution in the 2 : 1 mixture of acetone and acetyl chloride, while the solubility of the strontium chloride turns upon the amount of water originally present—that is, upon the development of hydrogen chloride.

It appears, therefore, that the method which rests upon the action of a 4 : 1 mixture of acetone and acetyl chloride upon the concentrated solution of the chlorides affords easy and exact means for the separation and estimation of barium associated with calcium and magnesium. It is not recommended for the separation of barium from strontium.

—*American Journal of Science*, xxxii., 212.

#### Extraction of Gases from Copper. —Marcel Guichard.

—The author's experiments show that commercial copper may contain dissolved gases (CO<sub>2</sub>, CO, N, H), which will cause an error of several thousandths in determinations of oxygen carried out with the metal. More accurate results may be obtained by using a large surface of the metal and previously heating it for a long time to 600°. Copper wire about 0.1 mm. in diameter is suitable.—*Bull. Soc. Chim. de France*, xi.—xxii., No. 3.

## THE DETERMINATION OF VANADIUM IN VANADIUM AND CHROME-VANADIUM STEELS.\*

By J. R. CAIN.

### Introduction.

VANADIUM has been called by metallurgists a "homœopathic" remedy because of the remarkable results obtained by small additions of it to other metals, notably to steel. Carbon steels or alloy steels as produced in this country, when they carry vanadium, usually contain from 0.10 to 1.00 per cent. It has been claimed by some that the element acts by removing dissolved gases, especially nitrogen, from the molten steel, with resulting elimination in the slag of the greater part added, and that the amount left in the steel itself is of secondary importance. However, others have shown that the microscopic structure of steel is greatly modified by the residual vanadium in the amounts in question here, and, as might be expected, there are corresponding changes in physical properties. Hence it will be seen that a high degree of accuracy in determining vanadium in steel is to be desired. Considerations such as these, combined with requests from many sources, led the Bureau of Standards to undertake the preparation of a vanadium standard steel similar to the analysed plain carbon steels which it has issued for some time. In conformity with the usual practice of the Bureau, samples were analysed by its chemists and by prominent technical and works chemists (eleven in all). The first figures thus obtained for vanadium were so unexpectedly discordant as to indicate sources of error in methods used which had probably been overlooked or unrecognized. Accordingly, some of the most probable of these were investigated by the Bureau. The results of this investigation were communicated to those participating in the co-operative work, and a satisfactory concordance in the final vanadium figures was very soon obtained. Inasmuch, as some of these sources of error do not seem to have been sufficiently emphasised in the literature, concise statements regarding them may be of service. Three classes of methods were used by the co-operating analysts:—

*Class A.*—Methods like that first described by Campagne (*Ber.*, 1903, xxxvi., 3164), and found with little variation from the original in many text-books on steel analysis. The hydrochloric acid (ferric) solution of the steel is extracted with ether, which removes most of the iron, leaving the vanadium in the aqueous layer. This portion is evaporated to dryness, and the operation repeated two

\* *Journal of Industrial and Engineering Chemistry*, iii., No. 7.

or three times with fresh portions of hydrochloric acid. The latter reduces the vanadium to the quadrivalent state; the final evaporation is made with sulphuric acid, and is continued until fumes are given off strongly. The solution is then titrated against permanganate.

**Class B.**—Methods depending upon the reduction of quinivalent to quadrivalent vanadium by ferrous sulphate, either by titrating directly against a ferrous solution or adding excess of the same and titrating back with bichromate; potassium ferricyanide is used either as an external indicator or by adding it directly to the solution undergoing titration.

**Class C.**—Most of the iron is extracted as under Class A, the hydrochloric acid replaced by nitric acid, and the vanadium separated from iron, chromium, &c., by pouring into a boiling solution of sodium hydroxide. The vanadium goes into the filtrate, and is precipitated by mercurous or lead salts, the final estimation being either gravimetric or volumetric.

It seems likely that these three classes of methods comprise those most used in this country, inasmuch as the group of co-operating chemists was typical. The same methods are used with little or no change for the analysis of chrome-vanadium steels carrying usually from 0.2 to 5 per cent chromium.

#### Some Sources of Error.

**General Errors.**—An error in all methods where final titration is made against permanganate may arise by failure to deduct the blank caused by the presence of elements other than vanadium; this may be particularly high in such methods as that of Campagne, where, if the ether extraction is not carefully done, there may be large amounts of ferric sulphate present during the titration. Campagne himself speaks of this point (*loc. cit.*), but it is not usually mentioned in text-books. If salts yielding green or blue solutions are present these may obscure the true end-point, requiring several tenths of a cc. of tenth-normal permanganate in excess. Indeed, in low vanadium products the blank may be much larger than the amount required by the vanadium, or if the analyst does not make a qualitative test for vanadium he may report its presence when the steel contains none. Another point to be observed is the temperature of the solution being titrated. The optimum temperature is 70–80° C. (Hillebrand, "Analysis of Silicate and Carbonate Rocks," *Bull.* 422, p. 151, U.S. Geol. Survey). It is almost impossible to secure a good end-point in a cold solution. On the other hand, the work of Sarkar and Dutta (*Zeit. Anorg. Chem.*, 1910, lxvii., 225), and of others on the reduction of permanganate by hot sulphuric acid solutions of manganous sulphate shows the importance of not titrating at too high a temperature.

**Errors Incident to Methods of Class A.**—(1). During the ether extraction there is almost always some iron reduced to the ferrous condition; this is not always re-oxidised during the course of the analysis before the titration, and therefore might be calculated as vanadium if this fact is not taken into consideration.

(2). The ether, or impurities in it, may act on the strong sulphuric acid when the solution is evaporated to small volume with this acid. There are, then, present substances which may act on permanganate. In the laboratory of the Bureau of Standards, Washington, separation of carbonaceous material has been observed at this stage, with accompanying odour of sulphur dioxide.

(3). The addition of sulphuric acid before the solution has been repeatedly evaporated with fresh portions of hydrochloric acid is to be avoided, because, if the sulphuric acid is added before reduction of vanadium to the quadrivalent state has been attained, the reduction is likely to be incomplete.

(4). If the evaporation with strong sulphuric acid is too prolonged or carried out at too high a temperature the reverse reaction, resulting in the oxidation of vanadium tetroxide to vanadium pentoxide by the sulphur trioxide,

may take place (Koppel and Behrendt, *Zeit. Anorg. Chem.*, 1903, xxxv., 156).

(5). No other metals capable of oxidation to higher valence by permanganate should be present. Those most likely to be encountered in steel analysis are chromium, molybdenum, and tungsten. The latter two may be removed before titration without great difficulty; the methods hitherto given for separating vanadium and chromium are so labourious that this precaution is often omitted in the case of chromium. A correction for the latter is invariably necessary, particularly in some steels where the chromium and vanadium may be present in the ratio of twenty or forty to one. Moreover, the amount of chromium oxidised to chromic acid is greater when titration is made at 70–80°, as is imperative for a good vanadium end-point, than where the solution is titrated cold, as is sometimes recommended. For details regarding this correction for chromium see "Analysis of Silicate and Carbonate Rocks" (Hillebrand, *Bull.* 422, p. 152, U.S. Geol. Survey).

**Errors Incident to Methods of Class B.**—Methods requiring the use of ferricyanide as indicator for ferrous salts, when quadrivalent vanadium and ferrous salts are also present, must of necessity be very uncertain, yet these are the conditions under which the determination is carried out. The reason for this is very evident when it is remembered that ferricyanide in acid solution rapidly oxidises quadrivalent vanadium to the quinivalent condition with resulting production of ferrocyanide. The latter reacts at once with the ferric iron, so that a blue colour is present in the drops of indicator as soon as an appreciable amount of vanadium is reduced and long before the colour due to excess of the titrating solution makes its appearance. Consequently, such methods, if at all applicable, must yield results varying with the operator and requiring arbitrary and uncertain correction factors. Much difficulty was experienced in attempting to determine vanadium in pure vanadium solutions by this method; the reason for this, as stated above, was soon discovered, and later, references to the same matter were found in the literature (Campagne, *loc. cit.*; Brearley and Ibbotson, "Analysis of Steel Works Materials," p. 89).

**Errors Incident to Methods of Class C.**—Vanadium is almost always carried down by the precipitate of ferric and chromic hydroxides, &c., upon pouring into sodium hydroxide. Usually two or three precipitations are necessary to obtain all the vanadium in the alkaline filtrate. The difficulty seems to be largely due to the presence of manganese, which, of course, the ether does not extract, for by working in the absence of manganese it has been found possible to make good separations with one precipitation. However, there is no simple method for removing manganese at this stage of a vanadium determination in steel without introducing other complications. If chromium is present another difficulty is added, for part of the manganese is oxidised by the air, and precipitated while the sodium hydroxide solution is being boiled to secure complete precipitation of chromium and complete extraction of vanadium from the precipitated hydroxide; this peroxide rapidly oxidises some of the chromium to chromate, which goes into the filtrate with the vanadium. If the sodium hydroxide precipitation is repeated, or a third precipitation is necessary, as may happen, a very large amount of chromium goes into the filtrate. In fact, the first operation leaves enough chromium with the vanadium to introduce serious error in determining the latter unless a correction is made; furthermore, the same cause may require appreciable correction to be applied to the chromium. The addition of sulphurous acid to the acid solution of the steel just before it is poured into the alkali, as is recommended sometimes, does not help, for of course it is not effective after the solution is strongly alkaline. Another source of trouble is the organic matter mentioned above as sometimes coming from ether; this causes appreciable amounts of iron and chromium to dissolve in the filtrate with the vanadium. It is evident that



all of the sources of difficulty, except the last mentioned, are present in even greater degree when an attempt is made to carry out the caustic soda separation without a preliminary extraction of most of the iron by ether. Thus it will be seen that to separate the vanadium from the iron and to obtain all of it in the filtrate may be, and usually is, a long and complicated operation. When this is accomplished there may be present a large amount of chromium, and this occasions another series of difficulties, for the chromate precipitates with the vanadate, whatever the method of precipitation. The only alternative is to titrate the vanadium in presence of the chromium, making the uncertain corrections above mentioned, or to make an electrolytic separation as described later.

When attempt is made to extract vanadium from steel by fusion of the oxides obtained by evaporation and baking a nitric acid solution of the metal, an old method which is now probably little used for this class of material, the same series of difficulties as enumerated under Class C is encountered. It seems almost impracticable to extract quantitatively, say, one-tenth of 1 per cent of vanadium in this manner without undue expenditure of time and labour.

It is clear, then, that there are marked defects in the most commonly used methods for determining vanadium in steel, unless the analysis is conducted with extreme care, requiring more time than is usually available in a technical laboratory, or unless the analyst is so experienced that he can recognise and correct for disturbing factors. Accordingly, the present research was started with the hope that a simpler and more accurate procedure might be outlined, and one which would at the same time be reasonably short.

#### *Preliminary Work toward a New Method for Vanadium.*

Much work was done with the idea of determining vanadium without a preliminary separation from iron. It seemed possible that the vanadium might be oxidised to vanadate and then reduced by hydrobromic acid by distilling in an apparatus suitable for collecting the liberated bromine in alkali. The difficulty, however, is to secure oxidation of the vanadium, and then get rid of the excess of oxidiser without at the same time reducing some vanadic acid. It was found that the vanadium of a dilute sulphuric acid solution of a vanadium or chrome vanadium steel could be oxidised easily enough in the cold by manganese dioxide with out converting any noticeable amount of chromium to chromate, the excess of manganese dioxide being eliminated by filtration. But when such a solution was placed in the distilling apparatus and distilled after the addition of a large excess of hydrochloric acid and potassium bromide, as recommended by Edgar (*Am. Journ. Sci.*, 1909, xxvii., 174), there was almost always more bromine liberated than corresponded to the vanadium present. Many efforts were made to get rid of the disturbance, such as long boiling of the oxidised steel solution before placing in the distilling apparatus, reduction of the amount of sulphuric acid used for solution to the minimum necessary, &c., but while the results were usually as accurate as those obtained by any of the methods above described there were occasional and unexplained irregularities which finally led to the abandonment of the method for technical purposes. This is regrettable, for, theoretically, such a procedure is ideal; practically it would be extremely short and simple. It seems likely that the trouble experienced was due either to the known solubility of manganese dioxide in sulphuric acid or to the action of sulphuric acid itself on the hydrobromic acid in the strongly acidified solution in the distilling flask.

From this it appeared desirable to develop a method which would obtain the vanadium in a solution free from all other metals, so that one might always be certain that the oxidising or reducing action, whichever is made the basis of a volumetric method, is exerted by vanadium compounds and nothing else. The manner of accomplishing this was suggested in part by a dissertation of Albert Steffan ("Ueber die Bestimmung von Kleinen Mengen an

Chrom und Vanadin in Gesteinen und Stahlarten," Zurich, 1902), who used barium carbonate for precipitating vanadium and chromium, together with relatively little iron, from the (ferrous) solution of the steel. The principle at the base of the method has long been applied to other separations. It has invariably been recommended until recently to conduct this precipitation in the cold, shaking frequently and allowing to stand for many hours. It has been found, however, by numerous experiments here that a few minutes' boiling with the carbonate will completely precipitate much larger amounts of vanadium and chromium than are likely to be encountered in steel analysis; furthermore, the precipitates are free from manganese, a distinct advantage from many standpoints over the ether separation. The shortening of the time required for precipitation when solutions are boiled has recently been noted by others in connection with steel analyses; also the use of zinc oxide as a precipitant (Slavik, *Chem. Ztg.*, 1910, xxxiv., 648). The precipitate obtained in this way contains the insoluble matter from the solution of the steel, a little iron, all the chromium and vanadium, and a considerable excess of the precipitant. The vanadium and chromium may be extracted by fusion with sodium carbonate, but the barium holds vanadium tenaciously, and more than one fusion is usually necessary, so that this way of handling the precipitate, although apparently simpler, is longer than the one to be described later.

Smith ("Electro analysis," Fourth edition, p. 258) describes an electrolytic method for separating vanadium from iron by driving the latter into a mercury cathode, and in another section he gives directions for electrolytically precipitating chromium under practically the same conditions, hence it appeared feasible to separate both iron and chromium from vanadium by electrolysis when the three are together. Preliminary experiment showed this to be possible, and it was then decided to dissolve the precipitate mentioned above in appropriate manner, and submit it to electrolysis in order to obtain a pure vanadium solution. It seemed desirable, however, to be rid of the excess of the precipitant before electrolysis. The necessary excess being relatively large, it would take too long to drive the iron and chromium out of solution if the precipitant were to accompany them into solution and be deposited along with them, as would be the case with zinc oxide, for instance. Moreover, it seemed desirable to dissolve the steel in sulphuric acid, as the electrolytic deposition is made from sulphate solution. This, of course, made inconvenient the use of barium carbonate as precipitant. It was therefore decided to try the suitability of cadmium carbonate for the purpose, with the idea of throwing out the excess of cadmium by hydrogen sulphide from the acid solution of the carbonate precipitate. This method gave entirely satisfactory results; the rate of precipitation of the vanadium and chromium seems even more rapid than with zinc oxide or barium carbonate. The precipitate of cadmium sulphide obtained in a boiling very slightly acid solution is easily filtered, and never carries down vanadium.

The precipitation of vanadium and chromium from a reduced and boiling solution of steel by any of the precipitants herein mentioned succeeds equally well in hydrochloric or sulphuric solutions, but seems to proceed a little faster with cadmium carbonate and a sulphate solution.

(To be continued)

#### THE PAY OF THE PUBLIC ANALYST.

THE remuneration of the public analyst has seldom been upon a scale consistent with the training, skill, and experience which are required of him, but now that the practice of adulteration is becoming such a refinement, requiring a very elaborate series of operations for its detection, the scale of fees in many instances is wholly inadequate. There can be little doubt that modern methods

of adulteration are often the product of a subtle scientific mind which discredibly turns its attention to the possibilities of eluding the control over the purity and quality of food, drugs, and drink provided by the Sale of Food and Drugs Acts. No analyst nowadays, if he is an honest man, dare certify that a sample, say, of butter, is genuine without determining not only the amount of butter-fat present, but the nature of the fat also, a process which involves considerable skill and attention. Then he will estimate the amount of water, curd, salt, and will search for preservatives, of which there are so many, and when found he will be bound to estimate the quantity in order to be able to say whether that is permissible. He is expected to do all this for, say, 10s. 6d. It may be urged that some compensation is arrived at because other samples which come before him may include substances which give very little trouble, so far as their analysis is concerned. Accepting that for a moment, we doubt then whether the average fee for analysis is a fair remuneration for the high qualifications now required for the post. The days when 10s. 6d. was an ample reward for casting a specimen of suspect coffee upon the surface of water and noting whether some of the particles rapidly sank, colouring the water on their downward way, which meant the presence of chicory, are gone. The public analyst's work now is work of the highest scientific order; it must be done by a competent and conscientious man, otherwise the administration of the food laws must soon fall into disrepute. Slovenly practice must be impossible if discredit of the public analytical service is to be prevented. And there should be no temptation in the shape of totally inadequate pay to shirk the carrying out of a duty in a thorough and effective manner. The machinery which guards the purity and quality of our food supply must be efficient, and it is impossible to purchase efficiency at rates which are so low as to give no recompense for training, skill, and responsibility. Only recently advertisements have come to our notice which invite qualified analysts to apply for a post which involves the analysis of 800 samples of foods and drugs per annum, and the remuneration offered is an annual sum of £150. In another instance the analyst is required to provide and maintain a laboratory himself, together with apparatus, chemicals, and assistance "as are necessary to enable him adequately and completely to execute the duties of the office." (The italics are ours) The work means examining and reporting upon 2000 samples, formal and informal, per year, and the remuneration offered is £500. The "informal" samples might mean the performance of some very elaborate analyses indeed, which at 10s. per analysis could not possibly meet the expenses of the "apparatus, chemicals, and assistance" laid down in the advertisement. The living wage is left entirely out of the proposition, and such a policy must sooner or later bring discredit upon a very important department of public service.—*The Lancet*, March 9, 1912.

**The Royal Photographic Society of Great Britain.**—An interesting collection of photographs is now on view at the Royal Photographic Society's House, 35, Russell Square, W.C. The photographs are views among the mountains surrounding St. Moritz, in the passes and in the neighbouring countries. The author of them, Mr. G. R. Ballance, has exercised his artistic taste in selecting the most picturesque views, and his work will recall to many visitors the scrambles they have enjoyed among the weather-splintered peaks. The mountain flora is depicted, and here and there the wayside shrines commemorating the toll of lives exacted from the Alpine adventurers. Leaving the mountains this artist carries the spectator through Tivoli to the Italian plains and the lagoons of Venice, with many a beautiful scene *en route*. The Exhibition is open free to the public on presentation of visiting card, daily from 11 a.m. till 5 p.m. (Saturdays 11 a.m. till 2 p.m.), from the 6th inst. till April 20th.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

Ordinary Meeting, February 29th, 1912.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"*The Bacterial Production of Acetylmethylcarbinol and 2:3-Butylene Glycol.*" (II.). By Dr. ARTHUR HARDEN, F.R.S., and DOROTHY NORRIS.

Père considered that glyceraldehyde was produced during the bacterial fermentation of sugars, and advanced the hypothesis that all sugars undergoing such decomposition were primarily broken down to glycerose.

The authors have repeated his experiments and find that the volatile reducing and laevorotatory substance which he considered to be glyceraldehyde is in reality acetylmethylcarbinol. Hence the above hypothesis cannot be considered as proved.

A quantitative examination has been made of the products formed by the action of *B. lactis aerogenes* (Escherich) on glycerol under anaerobic conditions. These consist of ethyl alcohol and formic acid comprising 60 per cent of the whole, together with smaller quantities of acetic, lactic, and succinic acids and 2:3-butylene glycol, carbon dioxide, and hydrogen.

"*Instrument for Measuring the Distance between the Centres of Rotation of the Two Eyes.*" By H. S. RYLAND and B. T. LANG, F.R.C.S.

The apparent position of a pin fixed at a known distance in front of a scale is taken with each eye singly. The operation is repeated with the pin at a different distance, the other conditions remaining unaltered. From the data thus obtained the distance between the centres of rotation of the two eyes can be calculated. The result is independent of variations in the distance between the pupils, and the process can be applied in cases of squint. In an alternative method three pins in a row parallel to the scale are used.

"*Locomotor Function of the Lantern in Echinus, with Remarks on other Allied Lantern Activities.*" By J. F. GEMMILL.

"*The Relation of Wild Animals to Trypanosomiasis.*" By Capt. A. D. FRASER, R.A.M.C., and Dr. H. L. DUKE.

*Trypanosoma uniforme* was the only species of trypanosome obtained as the result of examination of wild animals, including 32 Lake-shore antelopes.

The available evidence points to bush-pig, crocodile, monitor, frog, and fowls being refractory to *Trypanosoma gambiense*.

The edible rat, which is susceptible to *T. gambiense*, can, by virtue of its habits, be of little importance in considering the question of a reservoir.

"*Transmission of Trypanosoma nanum (Laveran).*" By Dr. H. L. DUKE.

This trypanosome can be transmitted by *Glossina palpalis*, the proportion of positive flies obtained being relatively large, and indicating that this fly may play an important part in the spread of the disease in Uganda.

"*Development of a Leucocytozoon of Guinea-pigs.*" By E. H. ROSS.

The paper describes an investigation of some remarkable structures found in the mononuclear leucocytes (lymphocytes) of the blood of guinea-pigs; they are known as "Kurloff's bodies." There has been considerable controversy regarding the nature of these bodies, some authorities describing them as vacuoles containing secretion products, some as symbiotic structures, as chlamydozoa, as cytocytes, as parasites, and as spurious parasites.



By a new technique for *in-vitro* staining, known as the jelly method, the minute structure of these bodies can be seen, while the lymphocytes which contain them are stained alive. The method shows conclusively that Kurloff's bodies are living parasites.

The method also shows how the bodies develop within the lymphocyte host, for the chromatin within them stains in the various phases, and the whole development can be followed from the earliest Leishmania-like inclusion in the leucocytes until ultimately the leucocytozoon is seen to contain a mass of spirochete-like bodies which have been likened to *gametes*. The blood of such guinea-pigs shows, when examined with the dark-ground illumination, free swimming spirochetes; and these have been fixed and stained. The details of the jelly method are described.

# SOCIETY OF CHEMICAL INDUSTRY. (LONDON SECTION).

Ordinary Meeting, March 4th, 1912.

Mr. E. GRANT HOOPER in the Chair.

THE following papers were read and discussed:—

"Photographic Process." By Dr. C. E. KENNETH MEES.

The history and development of the photographic industry is traced from the days not very long ago when the factory was a purely domestic concern worked by the owner and his family as a secret concern, to the present time when tons of bromide and enormous quantities of silver and glass are used and the daily output of papers amounts to miles.

The chemical nature of the process, so far as it concerns the light-sensitive properties of salts of silver, is considered in relation rather to the factory process of emulsion making than the theory of the latent image or of the process of development.

The organisation of factories for both plate and paper making is described and the many ancillary operations indicated.

The methods of testing the products of the industry with a view to securing uniformity of output are considered in historical sequence from the test of a preliminary exposure and development of plates, or printing from a negative with papers to be tested to the sensitometers of Warnerke (1881) and Hurter and Driffeld (1890). The lack of uniformity in the speeds assigned by different makers to their plates is partly due to the fact that lights which are photometrically equal are not necessarily so photographically, and the need of a satisfactory standard is felt.

"Estimation of Glucose in Leather." By J. GORDON PARKER and J. R. BLOCKLEY.

When, in the Von Schroeder method, normal lead acetate is used for the determination of the water soluble matters, a higher percentage of glucose is obtained than if the basic acetate is used.

It appears probable that a cause of the discrepancy may be the imperfect removal of gallic acid by the normal acetate, since the solutions of water soluble matter are usually acid with acetic or lactic acid, and it is known that gallic acid is not completely removed by lead acetate in acid solutions. Gallic acid has a reducing action on Fehling's solution, although the reverse is sometimes stated, and hence increases the apparent amount of glucose.

Experiments with made-up solutions, neutralised immediately before the addition of the acetate, seemed to indicate the above facts; this, together with the acid neutralising power of basic lead acetate, would account fully for the discrepancy, but experiments with neutralised leather solutions showed that the results were still discrepant, but to a less extent.

# SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, March 6th, 1912.

Mr. LEONARD ARCHBUTT, President, in the Chair.

Miss Maud Gazdar and Mr. Herbert Hawley were elected Members of the Society.

Certificates were read for the first time in favour of Messrs. Reginald Freeman Easton, 38, Edith Road, West Kensington, W.; and Leonard Goodban, 43, Addison Gardens, W.

Certificates were read for the second time in favour of Messrs. Maurice E. Balston, Howard A. Caulkin, and Charles Reginald Wilkins.

The following papers were read and discussed:—

"Method of Estimating Calcium Carbonate in Soils." By HERBERT S. SHREWSBURY.

The author treats 10 grms. of fine air-dried soil in a stoppered wide mouthed flask with 100 cc. of roughly quarter normal acetic acid, rotating the flask every time most of the soil settles, during ten minutes.

The same weight of soil is treated in the same manner with 100 cc. of distilled water. 25 cc. of the filtrate from each extraction are evaporated in a platinum dish, ignited at a bright red heat for thirty minutes, and the residues of (principally) lime dissolved in 10 cc., or more if necessary, of decinormal acetic acid. Back titration with decinormal soda or potash and phenolphthalein gives the cc. equivalent to the lime in the residues. Subtracting the volume obtained from the control (which will not exceed 0.1 cc. in most soils), the remainder multiplied by 0.2 gives the percentage of calcium carbonate in the soil. The control experiment eliminates such bodies as the carbonates or organic salts of the alkalis, soluble organic calcium salts, calcium nitrate, &c. Acetic acid is chosen for the titration as it does not dissolve ignited iron oxide. Test experiments with four different soils gave the following percentages of calcium carbonate in the soil:—

| Original | Added. | Total. | Found. |
|----------|--------|--------|--------|
| 0.07     | 0.05   | 0.12   | 0.13   |
| Nil      | 0.50   | 0.50   | 0.50   |
| 0.29     | 0.50   | 0.79   | 0.61   |
| 0.23     | 4.76   | 4.99   | 4.86   |

"Standards for Malt Vinegar." By A. CHASTON CHAPMAN.

The author shows that malt vinegar, that is to say, vinegar complying with the requirements of the United States Department of Agriculture in respect of its mode of manufacture, may nevertheless give analytical results well outside the standards laid down and adopted by the Department. Thus, it is shown that in cases where fermentation has been very completely effected, the malt vinegar may have a *lævo*-rotatory instead of a *dextro*-rotatory action on polarised light, owing to the disappearance of the *dextro*-rotatory carbohydrate matters, and to the presence of *lævo*-rotatory proteins.

It is also pointed out that in the case of malt vinegars made with hard water the proportion of soluble phosphoric acid may fall much below the limit laid down in the Department's regulations.

Illustrative experimental results are given.

"Estimation of Ammonia in Carbonated Waters." By G. D. ELSDON and NORMAN EVERS.

The authors having noticed that the amount of free ammonia found in carbonated waters was often small, even in the case of obviously bad waters, have shown that the presence of carbon dioxide in the distillate in quantities greater than 5 parts per 100,000 seriously interferes with the colour produced by Nessler's solution.

From an examination of waters aerated in the laboratory it was found that an aerated water containing as much as

0.020 part of free ammonia per 100,000 might, if treated by the ordinary method, be returned as practically ammonia free.

The following process is proposed as the most satisfactory method of overcoming this difficulty. After removal of as much carbon dioxide as possible by shaking in a Winchester, 500 cc. of the water are transferred to the distillation flask, and 5 cc. of  $\text{NH}_2\text{SO}_4$  (or more if the alkalinity of the water requires it) are added. 50 cc. are then distilled off and rejected, thus removing the carbon dioxide. An equivalent quantity of  $\text{N}/\text{NaOH}$  and the usual amount of sodium carbonate are then added, and the estimation of free and albuminoid ammonia proceeded with in the usual manner.

Many waters were aerated in the laboratory, and examined by this process. The results on the aerated waters were practically identical with those on the original waters as regards free ammonia.

The albuminoid ammonia is slightly increased by aeration, whether it is estimated by the above process or by the ordinary method.

*"New Preservative for Milk, Cream, &c. (Mystin)."*  
By GEORGE A. STOKES:

Mystin, a new milk preservative, it is claimed cannot be detected by analysts. It consists of formaldehyde and sodium nitrite; the latter renders any of the usual tests for formaldehyde useless. The nitrite, however, is indicated by most of the methods for fat determination (such as the Gerber and Schmidt). In such case distillation with phosphoric acid sets formalin free.

*"Phosphomolybdate Estimation of Phosphoric Acid in Soils."* By S. J. M. AULD.

Examination of the various methods for utilising the bulky ammonium phosphomolybdate precipitate for the estimation of small quantities of  $\text{P}_2\text{O}_5$  in soils, &c., has led to the conclusion that the direct weighing of the precipitate should be avoided, and that, if used, the factor in Carnot's method should be 0.0378.

The different factors given for the  $\text{P}_2\text{O}_5$  content of the residue obtained after evaporation and heating the ammoniacal solution of the yellow precipitate are probably due to decomposition occurring to a rather indefinite extent both on dissolution of the precipitate in ammonia and on heating the residue.

The best results have been obtained by re-precipitating the ammoniacal solution with nitric acid and a little more ammonium molybdate solution, after which the precipitate is collected in a Gooch crucible and ignited until of a uniform blue colour, and of constant weight. The factor to be used is 0.0396. This corresponds to a compound of the formula  $\text{P}_2\text{O}_5 \cdot \text{Mo}_3\text{O}_8 \cdot 21\text{MoO}_3$ .

## THE INSTITUTE OF CHEMISTRY.

### IMPORTANT NOTICE.

THE Council of the Institute of Chemistry of Great Britain and Ireland have had under consideration the particulars of proposed appointments of Public Analyst for the Metropolitan Boroughs of Lambeth and Wandsworth.

In each of these cases the following terms are set forth:—

"3. The officer will be required to examine and report upon 2000 samples, formal and informal, or such number, up to the said 2000, as may be submitted by or on behalf of the Council in every year. For the purpose of this clause, a year shall be held to commence on January 1st and end on December 31st."

"4. The officer will be required, at his own cost, and in such place as the Council may approve, to provide and maintain his own laboratory, together with all such apparatus, chemicals, and assistance as are necessary to enable him adequately and completely to execute the duties of the office. The officer will also be required to

provide, at his own cost, and to the satisfaction of the Council and the approval of the Local Government Board, a competent deputy to act during any absence from duty of the officer through sickness, holiday, or other cause."

"5. In addition to the certificate of analysis directed by the Sale of Food and Drugs Acts to be given to the person submitting a sample, the officer will be required, at the same time as he gives the Statutory certificate, to transmit direct to the Medical Officer of Health a duplicate copy of every such certificate."

"6. The fixed remuneration to be paid by the Council in respect of the said 2000 samples, or such number up to 2000 as may be submitted in any year, will be £500 per annum, and will be payable quarterly on March 31st, June 30th, September 30th, and December 31st in every year."

The terms in the case of Wandsworth contain a further clause:—

"7. The fee of one guinea will be paid by the Council for each analysis of water and one guinea for each attendance of the officer at the police-court when required by the Council."

The Council have also considered an announcement regarding the proposed appointment of an Analyst to the County of Antrim, under the following conditions:—

"The Analyst will be paid a salary of £150 per annum, with first-class travelling expenses through the County when he is required as a witness in any case of prosecution."

"He is to make analyses of all samples submitted to him by the Inspectors appointed under the Foods and Drugs Acts, and to analyse samples under the Fertilisers and Feeding Stuffs Act, 1906, for farmers and others resident in the County, at a fee of 5s. for each analysis, payable by the person sending the sample."

"Three months' notice on either side to terminate the engagement."

In explanation of the above, the Registrar has received the following letter from the Deputy Secretary to the Antrim County Council:—

"In reply to yours of the 19th inst., I beg to inform you that the salary of £150 per annum to be paid to the County Analyst for County Antrim is for his services in making analyses of samples taken under the Sale of Food and Drugs Act. In addition to this salary he is to be paid a fee of 5s. for each analysis of samples under the Fertilisers and Feeding Stuffs Act, 1906. This fee to be paid by the farmers and other persons resident in the County, sending the samples."

"There is no limit to the number of samples likely to be submitted to the Analyst, so far as I am aware."

The number of samples per annum usually submitted is over 800. During the quarter ending September 30th, 1911, 270 samples were submitted for analysis.

The Council of the Institute are of opinion that the remuneration and conditions offered for the three appointments referred to above are not compatible with the adequate and complete execution of the duties of these offices, and that it is contrary to the public interest that appointments should be made on such terms.

The Council of the Institute view with the strongest disapproval the application for and acceptance of any of these appointments on the terms and conditions stated. They advise any Member who shall have made application for any of these appointments to withdraw the same; and they advise Members of the Institute to refrain from giving testimonials in support of any candidate applying for them.

By order of the Council of the Institute of Chemistry of Great Britain and Ireland, 30, Bloomsbury Square, London, W.C., March 1st, 1912.

RICHARD B. PILCHER,  
Registrar and Secretary.



## NOTICES OF BOOKS.

*Beiträge zur Technologie der Seife.* Vol. I. ("Contributions to the Technology of Soap"). By Dr. J. LEINDÖRFER. Dresden: Theodor Steinkopff. 1911. (1.80 Mk.).

THIS book is a reproduction of articles which have appeared in Volume II. of the "Kolloidchemische Beihefte," and discusses the technology of soap-making from the point of view of colloidal chemistry. It is devoted mainly to the consideration of preliminary experiments and to a discussion of the course of the saponification reaction, and is thus intended to lay a foundation for the second volume, in which the investigation of the raw materials of the soap industry will be treated in detail. A very slight knowledge of the phraseology and elementary facts of colloidal chemistry will enable the student to follow the text, which gives a clear *résumé* of the behaviour of fats and oils during saponification, the phenomena of coagulation, and dispersion agents.

*Monumentales und Dekoratives Pastell.* ("Monumental and Decorative Crayon Process"). By WILHELM OSTWALD. Leipzig: Akademisches Verlagsgesellschaft. 1912.

IN this brochure Prof. Ostwald publishes some information concerning the use of crayon in decorative painting, a technical process which he believes will have before it a useful future, when it has been perfected. For this end he earnestly asks for criticisms, both favourable and otherwise, of the process by all who have experimented with it. The pamphlet contains some practical details which have been communicated by artists as to the advantages of the process, and also gives a short account of the whole method, which the author has prepared in answer to the many letters which have reached him asking for details. In this account he explains the general principles, and gives some information concerning the preparation of different colours, methods of fixing, &c.

## CORRESPONDENCE.

### PROPOSED INDIAN ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

*To the Editor of the Chemical News.*

SIR,—The rapid expansion, during recent years, of the teaching of science throughout India as well as the multiplication of laboratories in colleges and institutions designed for research purposes, has disclosed a lack of scientific organisation which calls for the attention of all those engaged upon education and research work in the country. The isolated worker in India is, for the most part, deprived of the help afforded by scientific reference libraries, and his difficulties are enhanced by the fact that he is removed from the European environment whence he draws in large measure his inspiration.

We feel that the disabilities under which science suffers in India would be in part ameliorated, and that an impetus would be given to research work by the establishment of some central organisation after the manner of the British Association for the Advancement of Science, whereby different workers throughout the country might be brought into touch with one another more closely. The attention of the society might be directed to every field of enquiry and to every aspect of scientific activity whether purely theoretical or applied to those numerous special problems offered by the Indian Empire and peculiar to its natural and economic conditions. The study of endemic diseases, of the conditions governing agriculture and forestry, of engineering problems in the tropics and sub-tropics, of the

natural products of plants and of the mineral resources of the country, all these subjects call for extensive and systematic research in the laboratories with which India is now equipped. Behind this there is the larger educational problem, that of presenting to the minds of the people the aims of science, its purpose and ideals, its value as an instrument of social and economic improvement.

The objects of the proposed society are similar to those of the British Association, and they cannot be stated better than in the words which form the preamble to the constitution of that body:—"To give a stronger impulse and a more systematic direction to scientific enquiry; to promote the intercourse of societies and individuals interested in science in different parts of the country; to obtain a more general attention to the objects of pure and applied science, and the removal of any disadvantages of public kind which may impede its progress."

It is to be noticed that co-operation with the activities of the society would not preclude the publication of results in European periodicals nor in departmental journals dealing with particular branches of research; its primary aim is to afford a medium of communication between workers in different parts of India. Accordingly, it is proposed to establish an association which shall hold an Annual Meeting (sectional or otherwise) in the more populous Indian towns, where papers might be read and discussed, the proceedings to be published in the form of an Annual Report. We invite your opinion as to the expediency of founding a society of this kind, and would be glad to know whether, in the event of its successful inauguration, you would be glad to support it on the general lines indicated above. The success of the scheme naturally depends upon the extent and representativeness of the support accorded to it. We hope to arrange an early meeting in Calcutta, where the details might take practical shape.

In conclusion, attention may be drawn to a most important aspect of the scheme, namely, that concerning the co-operation of Indians. We realise that the future of science in India depends upon the adequacy of the practical training which students receive in College laboratories, and, furthermore, that nothing is better calculated to increase its efficiency than the inculcation of research as the ultimate purpose of all scientific knowledge. It is unnecessary to point out how many and varied are the problems awaiting solution, and how intimately the social and economic future of India is bound up with the successful application of scientific methods to all the activities, whether agrarian or industrial, of the community. We cordially invite the participation of Indian scientists, convinced in the belief that in such measure as it is accorded the objects of the society shall more nearly approach fulfilment and its usefulness and permanence be assured.

The undersigned, who in response to a public demand for action are undertaking the task of arranging an informal plebiscite on the question, would be glad of the favour of an opinion, and request that replies be sent to either of the addresses indicated below.—We are, &c.,

P. S. MACMAHON, M.Sc.(Man.), B.Sc.(Oxon.),  
Professor of Chemistry, Canning College, Lucknow.  
J. L. SIMONSEN, D.Sc.(Man.),  
Professor of Chemistry, Presidency College, Madras.

### ASSOCIATION OF CHEMICAL TECHNOLOGISTS ON THE PAY OF THE PUBLIC ANALYST.

*To the Editor of the Chemical News.*

SIR,—On behalf of the Association of Chemical Technologists, I beg to enter a strong protest against the course of action that is being followed by the Lambeth and Wandsworth Borough Councils in regard to the filling of the appointments of Public Analyst for those Boroughs, which have become vacant by the death of Dr. John Muter.

The terms of remuneration offered by both these Borough Councils are far below the lowest of the very inadequate rates of payment made to Public Analysts in London and throughout the country, and the acceptance of such appointments by a qualified scientific chemist on such terms would be degrading to the chemical profession and detrimental in the highest degree to the interests of the public. On the terms offered it is absolutely impossible that the responsible duties attaching to such appointments can be efficiently performed. A Public Analyst has great personal responsibility, his position is one of considerable anxiety, the value of his work is not generally understood, and the office he holds is widely disliked, for he is appointed under the provisions of Acts of Parliament which are extremely unpopular among certain sections of the community. It is therefore essential that he should be in a position of such independence that he may not be liable to influence or pressure from any persons whose interest it may be to prevent, as far as possible, the effective administration of the Acts. It must be remembered, too, that with the enormous increase in scientific adulteration, the work of a Public Analyst is to-day very different from the work required even ten years ago, and it is therefore all the more necessary that the general public for whose protection the Acts were passed should appreciate the advisability of preventing the ever-increasing attempts of local authorities of a certain type to reduce the remuneration of the scientific officers concerned to a level rendering the satisfactory discharge of their duties impossible.—I am, &c.,

J. WILBERFORCE GREEN, Secretary.

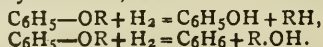
39, Victoria Street, Westminster,  
London, S.W., March 6, 1912.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Bulletin de la Société Chimique de France.*  
Vol. xi.—xii., No. 3, 1912.

**Preparation and Properties of Perchlorates.**—H. Goldblum and F. Terlikowski.—The perchlorates of nickel, cobalt, and didymium can be prepared by the action of perchloric acid on the respective carbonates, and that of chromium by dissolving the hydrate in the acid. The nickel salt thus obtained is a neutral salt of divalent nickel crystallising with five molecules of water. At 103° it decomposes, losing  $\text{HClO}_4$ , and yielding basic salts. In solution it undergoes hydrolytic decomposition. Cobalt perchlorate is very similar to the nickel salt, but it does not decompose when heated above 103°, nor does it undergo hydrolysis in solution. Didymium perchlorate is distinguished from the other salts by being less soluble in absolute alcohol.

**Decomposition of Mixed Phenolic Oxides in presence of Nickel and Hydrogen.**—A. Mailhe and M. Murat.—When oxide of phenyl is subjected to hydrogenation in presence of nickel the products are  $\text{C}_6\text{H}_6$ ,  $\text{C}_6\text{H}_{10}$ , and  $\text{C}_6\text{H}_{12}$ , with a certain amount of phenol, while the greater part of the oxide remains unaltered. Thus, phenyl oxide is very stable in presence of nickel. Some of it decomposes according to the equation  $\text{C}_6\text{H}_5\text{—O—C}_6\text{H}_5 + \text{H}_2 = \text{C}_6\text{H}_6 + \text{C}_6\text{H}_5\text{OH}$ . Phenol and benzene undergo consecutive hydrogenation over nickel, and at the temperature at which the reaction occurs the cyclohexanol is dehydrated with formation of cyclohexene, which is subsequently partially hydrogenated. With mixed ether oxides there is no hydrogenation of the nucleus at 350–380°. The ether oxide simply splits into phenol and hydrocarbon, or into benzene and alcohol,—



**Supposed Compound of Camphor with Naphthalene.**—M. Jouriaux.—The study of the fusibility of mixtures of naphthalene and camphor in all proportions shows that

no definite compound is formed. When a liquid mixture of camphor and naphthalene containing more than 42 molecules of naphthalene per cent is cooled, mixed crystals are deposited. Finally, at about 32.5° crystals, which differ greatly in appearance from the preceding, are formed. These constitute a eutectic. If the mixture contains more than 58 molecules of camphor per cent, on cooling the camphor solidifies in a transparent jelly containing less than three molecules per cent of naphthalene. This solidification is accompanied by a decided decrease of volume, and finally the eutectic crystallises.

### *Berichte der Deutschen Chemischen Gesellschaft,* Vol. xlv., No. 1.

**Triferro-carbide,  $\text{Fe}_3\text{C}$ .**—Otto Ruff and Erwald Gersten.—The authors have prepared triferrocarbide by mixing raw iron with lamp-black, heating to an intense white heat, and then turning the melt out on to an iron plate. It thus cools rapidly to a red heat, and subsequently cools more slowly. The hardness of the carbide thus obtained lies between 3.2 and 3.3, and thus it is not the hardness of the carbide itself which makes rapidly cooled steel hard, but that of its solid solution in  $\gamma$ -iron. The heat of combustion of  $\text{Fe}_3\text{C}$  is 2089.9 cal. per gm., and 375.1 cal. for 1 mol.  $\text{Fe}_3\text{C}$ . The heat of formation is –15.1 cal.

**Reaction between Iron Chloride and Pyrocatechin.**—R. F. Weinland and Karl Binder.—Iron chloride gives a dark red coloration with a concentrated solution of pyrocatechin in concentrated caustic potash. If ferric acetate is used instead of the chloride a similar dark red solution is obtained, and from it crystals of the compound  $\text{Fe}(\text{C}_6\text{H}_4\text{O}_2)_3 \cdot 2\text{H}_2\text{O}$  separate. Corresponding ammonium and sodium salts can be prepared. These compounds are the alkali salts of a pyrocatechin ferric acid,  $[\text{Fe}(\text{C}_6\text{H}_4\text{O}_2)_3]_3\text{H}_3$ , which is derived from the ferricyanide or ferrisulphocyanide residues by the replacement of six cyanogen or sulphocyanogen residues by three pyrocatechin residues. If a ferrous salt is substituted for the ferric salt the same compound is formed, the oxygen of the air converting the divalent into trivalent iron. Pyrocatechin behaves similarly towards other metals, e.g., aluminium, copper, nickel, cobalt, manganese.

## MEETINGS FOR THE WEEK.

- MONDAY, 18th.—Royal Society of Arts, 8. (Cantor Lecture). "Materials and Methods of Decorative Painting," by Noel Heaton, B.Sc.
- TUESDAY, 19th.—Royal Institution, 3. "Ancient Britain," by Thomas Rice Holmes, Litt.D.
- WEDNESDAY, 20th.—Royal Society of Arts, 8. "The Work of the Marine Biological Association," by F. Martin Duncan.
- Microscopical, 8. "Fairy Flies and their Hosts" (with Lantern Demonstration), by F. Enock.
- THURSDAY, 21st.—Royal Institution, 3. "Seasonal Dimorphism in Butterflies," by F. A. Dixey, F.R.S., &c.
- Royal Society. "Self-induction of Electric Currents in a Thin Anchor-ring," by Lord Rayleigh. "The After-luminosity of Electric Discharge in Hydrogen observed by Hertz," by Hon. R. J. Strutt. "Changes in the Dimensions of a Steel Wire when Twisted, and on the Pressure of Distortional Waves in Steel," by J. H. Poynting. "Critical Constants and Orthobaric Densities of Xenon," by H. S. Patterson, R. S. Cripps, and R. Whytlaw-Gray. "Experimental Work on a New Standard of Light," by W. A. Harwood and J. E. Petavel. "Distribution of the Scattered Röntgen Radiation," by J. A. Crowther. "Passage of Homogeneous Röntgen Rays through Gases," by E. A. Owen. "Fluorescent Röntgen Radiation from Elements of High Atomic Weight," by J. C. Chapman. "Nature of the  $\gamma$ -Rays Excited by  $\beta$ -Rays," by J. A. Gray.
- Chemical, 8.30. "Iso-erucic Acid," by A. K. Macbeth and A. W. Stewart.
- FRIDAY, 22nd.—Royal Institution, 9. "The North Sea and its Fisheries," by Prof. D'Arcy W. Thompson, C.B.
- SATURDAY, 23rd.—Royal Institution, 3. "Molecular Physics," by Sir J. J. Thomson, F.R.S., &c.



# THE CHEMICAL NEWS.

Vol. CV., No. 2730.

## REPORT ON THE MINERAL WATERS OF BATH.

By Prof. Sir WILLIAM RAMSAY, K.C.B., F.R.S.

SOME years after my discovery of helium in 1895, Lord Rayleigh made an estimate of the amount present in the gases escaping from the King's Well, and found that in 10,000 volumes of these gases there are 12 volumes of helium. Helium, like argon, is one of the "inert" gases, forming no chemical compounds, and therefore without any therapeutic action. Its presence in Continental mineral waters was demonstrated in 1896 by my then assistant, Dr. Travers, and myself, and M. Moureu, of the French Academy of Medicine, and M. Bouchard have made extensive researches on mineral waters, chiefly French, and have found helium to be present in larger or smaller quantity in many of them.

The cause of the therapeutic action of such waters has been obscure; mere artificial mixtures of the very ordinary salts which they contain have been said not to produce the same effects as the use of waters fresh from the springs; and it was not evident how the presence of helium, curious though it might be, could be credited with such beneficial results as are undoubtedly produced by "taking the waters."

But in 1903, in conjunction with Mr. Frederick Soddy, I solved the riddle by discovering that helium is one of the products of change of radium, and that its presence in the water is an indication that radium has been concerned in its production. As the chemistry of such substances is quite modern, perhaps a short explanation of what occurs may form a fitting preface to this report.

The element radium was discovered in 1898, in a hard black mineral named pitchblende, by Madame Curie. She has recently prepared the metal in minute quantity; it is a hard white metal, rapidly oxidised by air, and at once attacked by water; it closely resembles calcium, the metal of which ordinary lime is the oxide, and which is now manufactured on a semi-commercial scale. Like calcium, it forms salts, a few of which have been investigated; for instance, the sulphate and the carbonate, like those of calcium, are nearly insoluble in water; the chloride and the bromide are easily soluble. It is now being extracted from Cornish pitchblende in the works of the Radium Corporation at Limehouse in East London, and as bromide it meets with a ready sale at the enormous price of £20 per mgrm., equivalent to more than £500,000 per ounce. For the cure of rodent ulcer, and for certain skin affections, its curative effects are undoubted; and quantities of from 10 to 100 mgrms. are now being bought for use in hospitals and private practice.

Although an element, radium is unstable; that is, it is continually changing into another body, also "elementary." During this change it parts with helium, each atom of radium furnishing one atom of helium. As atom after atom of radium undergoes this change, miniature explosions take place, the effect being that atoms of helium are shot out with enormous velocity; they can be recognised by placing near the decomposing particle of radium a small screen of card, covered with a crystalline deposit of sulphide of zinc. As each atom of helium impinges on the screen, a flash of light occurs. That this is the case was discovered by Sir William Crookes; and Professor Rutherford, by counting the number of flashes, and by other means, too intricate to be described here, has succeeded in demonstrating that each atom of radium emits one atom of helium. These atoms of helium in rapid motion have been termed  $\alpha$  or alpha-rays. Their thera-

peutic effect is practically unknown; but they contain energy, or power of doing work, some twenty times greater than the other radiations termed  $\beta$  (beta) and  $\gamma$  (gamma) which also accompany the decomposition of the products of radium.

Having shot out its particle of helium, the atom of radium is no longer radium, but a gas, to which the name "radium emanation" was given by Prof. Rutherford and Mr. Soddy, but which, now that its properties and its atomic weight have been investigated, is better known as "niton." The rate of change of radium into niton is a very slow one. In theory, a given weight of radium should take an infinite time to change completely into niton and helium, because, as the decay goes on, less and less of the radium is left, and that smaller quantity gives off proportionately less niton and helium. In order to avoid the infinitesimal, it has been agreed to speak of the "half-period of decay," which is a perfectly definite interval of time. An ounce of radium, for example, after a period of 1760 years, would have half changed into niton and helium, while half an ounce of radium would be left unchanged. After a further period of 1760 years, half of the half-ounce, *i.e.*, a quarter of an ounce of radium, would be left, the other quarter-ounce having produced niton and helium. This process would go on indefinitely, and it is thus evident why the "half-period of decay" has been chosen as a means of measurement.

In collaboration, first with Mr. Soddy, and more recently with my present assistant, Dr. Whytlaw-Gray, I have investigated this gas, niton. Like argon or helium, it is inert, that is, it forms no chemical compounds. In another sense, however, it is not inert, for, as shown by Rutherford and Soddy, it itself has only an ephemeral existence; in 3'86, or say 4 days, it has half changed. As the activity of these substances depends on their rate of change, niton is a much more potent agent, weight for weight, than radium; indeed, the potency of radium may be ascribed to the extent of at least 75 per cent to the action of its product, niton.

Like all other gases, niton is compressible; it can be converted into a liquid at ordinary temperature by compression alone, and the liquid can be seen in a very narrow bore tube, as minute in bore as the finest needle is thick; naturally, a microscope must be used to see the liquid. It is colourless to look through, like water; like water, too, it freezes when cooled to a solid something like ice, I suppose; I say "I suppose," because it is impossible to see the solid as such. Solid niton causes the glass or silica tube in which it is necessary to confine it to glow with a brilliant light, comparable with that of a minute arc-light. The liquid, too, causes the glass to glow with a fairly bright violet light, so that if a tube containing it be looked at in the dark, the violet glow is considerable, but if looked through, against a light, the liquid niton is water-clear. Dr. Gray and I were successful in weighing this gas, and so in determining its atomic weight; this corresponds to the atomic weight of radium less that of an atom of helium; and we succeeded furthermore in weighing by difference the helium which the niton had produced in the course of its decomposition into further products.

I have stated that the half-period of decay of niton is about 4 days; in 8 days only a quarter is left; in 12 days an eighth, in 16 days a sixteenth, in 20 days a thirty-second, in 24 days a sixty-fourth, and in 28 days one 128th. Practically in a month it has all changed.

Its products, except helium which is a gas, are solids; they have been named "radium A, B, C, D," &c., by Prof. Rutherford. Two reasons have prevented their being investigated; first, their half-period of decay is too short; and they change before it is possible to handle them; and second, it is much easier to deal with a gas, owing to the much larger comparative volume which it occupies. But it is known that radium A, B, and C have short periods of decay, such that in three hours they have almost entirely changed into radium D. On the other hand, radium D

has a much longer half-period of decay, viz., about fourteen years, and no doubt it will be investigated. But from a therapeutic point of view it has little interest, for its change into further products takes place so slowly; and also without any rays.

The  $\beta$ , or beta-rays, are evolved during the change of radium into niton; and also during the subsequent changes of radium A and C into radium D. They are of a wholly different nature from the  $\alpha$ -rays; they are, to use ordinary language, not reckoned as an element, but are of the nature of negative electricity. Personally, I should be inclined to class negative electricity as a "substance," or as "matter"; but its properties are unique, and differentiate it from other varieties of matter. The "corpuscles," or atoms of electricity, now commonly termed "electrons," have been largely investigated; we owe much to the work of Sir J. J. Thomson, who has determined their approximate weight, and the velocity with which they move through space. They are identical, except in rate of motion, with the "cathode-rays" produced in the interior of a Röntgen-ray "tube" or bulb. When they are caused to impinge on an "anticathode" or piece of refractory metal, they produce what are commonly known as "Röntgen-rays," familiar to all by their power of penetrating flesh and blood, but not so easily bone.

It is the  $\beta$ -rays which have been chiefly used for therapeutic purposes. While  $\alpha$ -rays, that is, atoms of helium, like other gases, can be confined in glass or metal vessels,  $\beta$ -rays pass through; the amount passing naturally depends on the thickness of the walls of the vessel. The  $\alpha$ -rays, for example, given off from niton confined in a glass tube do not pass through the glass; the  $\beta$ -rays, due to the products of change of the niton, do pass through; and by interposing metal screens of foil of different thicknesses, a greater or smaller quantity may be allowed to impinge on the skin.

A third class of rays is also evolved, during the emission of  $\beta$ -rays, which have been termed  $\gamma$ -rays. It is not decided as yet what is their true nature. They have great penetrative power; indeed, three inches thickness of metallic lead is not sufficient entirely to stop them. They too are sometimes employed for curative purposes. It is suggested that they more resemble rays of light; that they are not "matter," but waves in the ether which surrounds and interpenetrates all matter.

*The Bath Waters.*—There are undoubtedly mineral waters which owe their curative power to what may be termed ordinary chemical ingredients; such are the sulphur waters of Harrogate, Strathpeffer, &c.; ferruginous waters of various spas; possibly arsenical waters, and those which contain lithium. But the recorded analyses of the Bath waters show, in the main, merely ordinary constituents, most of which are present in many drinking waters. Sulphates of calcium, of sodium, of potassium, carbonates of calcium and magnesium, are all common substances. The only unusual constituents of Bath waters; so far as the analysis made at the *Lancet* laboratory shows, are small quantities of strontium, of lithium, and a trace of bromine. But the fact that many mineral waters all over Europe have for ages been used for curative purposes, combined with our present knowledge that such waters, while not remarkable in "chemical" composition, all agree in yielding helium, the product of decay of radium, makes it particularly interesting to examine these waters for niton, as well as for radium itself.

Professor the Hon. R. J. Strutt has already informed the Baths Committee in 1903 of the presence of a trace of radium in the iron deposits left by the waters of the hot springs, as well as in the water itself. No estimations, however, appear to have been made.

In stating results it is convenient to give them as if the waters contained actual radium, even although none may be present as such, but only as niton. We have then all reduced to one standard. It may also be explained that a mgrm. is nearly the 30,000th part of an ounce, and that a cubic metre of water may be taken for the purpose of

visualising as a cubic yard, or, more accurately, as 30 cubic feet.

#### Facts Regarding the Bath Waters.

Density of the water from King's Well 1.0166  
Osmotic pressure equivalent to that of a  
salt solution containing per litre . . . 1.09 grm. NaCl

Volume of gas in 24 hours from—

|                  |                   |
|------------------|-------------------|
| King's Well ..   | 4927 litres       |
| Cross Spring ..  | 218 "             |
| Hetling Spring . | 218 " (estimated) |
|                  | 5363 "            |

Analysis of Gas (King's Well). Parts per 10,000 :—

|                    |      |
|--------------------|------|
| Carbon dioxide ..  | 360  |
| Nitrogen, &c... .. | 9640 |

No oxygen; no hydrogen; no marsh-gas.

The nitrogen contains :—

|           |       |
|-----------|-------|
| Argon ..  | 73.63 |
| Neon ..   | 23.34 |
| Helium .. | 2.97  |

From all three wells in 24 hours.—

|           |           |
|-----------|-----------|
| Argon ..  | 39 litres |
| Neon . .  | 12½ "     |
| Helium .. | 1½ "      |

#### Gases Dissolved in Pump Room Water.

This water contains 18.5 volumes of gas per 1000 of water. Its composition is :—

|                   |             |
|-------------------|-------------|
| Carbon dioxide .. | 6.9 volumes |
| Nitrogen ..       | 11.6 "      |

It had become somewhat aerated on drawing; but allowance has been made for that.

|                                            | Mgrms. per million litres. |
|--------------------------------------------|----------------------------|
| Radium in the water of the King's Well..   | 0.1387                     |
| Niton (radium emanation) in King's Well .. | 1.73*                      |
| Niton " Cross Bath . .                     | 1.19*                      |
| Niton " Hetling Bath ..                    | 1.70*                      |
| Niton " gas from King's Well               | 33.65*                     |

\* These figures are the weights of radium capable of forming the niton present in a million litres of water or gas.

I shall now proceed to comment on these facts.

*Osmotic Pressure.*—The significance of this measurement depends, I suppose, on the interchange of the salts in the water with the intestinal fluids; the salts will tend to pass from where the pressure is higher to where it is lower. I am, however, not competent to give an opinion on such a matter, which has a purely medical significance.

*Gas from King's Well.*—There are many remarkable features about this gas, one being the absence of oxygen. It occurred to me that it would be worth while to test this gas very completely for the presence of hydrogen and marsh gas; this was done by separating the volatile and non-condensable portion from half a litre of the gas; but it was found that neither was present.

The estimation of the total volume of gas was made for me by Mr. Jones, the Committee's engineer; but it appears to fluctuate with the barometric pressure, as well as by the amount of pumping which is going on. I have taken his figures as average ones; but no doubt observations over a considerable time should be made, in order to obtain a more certain average. It is very considerable, amounting to over 5 cubic metres in twenty-four hours.

The most noticeable fact about this gas is the enormous amount of neon which it contains. Neon is present in atmospheric air, which contains the following amounts of the inactive gases.



|              |                                | Ratio. |
|--------------|--------------------------------|--------|
| Argon . . .  | 93.2 volumes per 10,000 of air | 0.78   |
| Neon . . .   | 0.124 " "                      | 188.1  |
| Helium . . . | 0.0408 " "                     | 72.8   |

Under the heading Ratio is given the number by which the quantity of these gases in air must be multiplied so as to make them equal to the amounts of the gases in the gas collected from the King's Spring; thus, there is 188 times as much neon in the gas from the King's Spring as there is in an equal volume of atmospheric air.

Neon, I believe, has a certain commercial value, for it is used in filling vacuum tubes for testing the wave-length of the oscillations which serve in wireless telegraphy. There would be no difficulty in separating the neon from the Bath gas, if there proved to be a sufficient demand.

*Radio-activity of the Waters.*—My former student, Mr. Makower, has examined the radio-activity of the Buxton waters and gas. The water from the Hospital Natural Baths and from the Crescent Pump Room contain each 0.83 mgrm. per million litres; it will be seen that the water from the King's Spring and the Hetling Spring are more than twice as rich in niton; the Buxton water from the "Gentlemen's Natural Baths" contains 1.1 mgrm. per million litres, which is about the amount contained in the Cross Bath. The gas from the King's Spring contains over 33 mgrms. of niton per million litres; and this is about four times as much as is contained in the natural gas from Buxton, viz., 7.7 and 8.5 mgrms. per million litres.

It is, unfortunately, impossible to compare these amounts with statements of the radio-activity of foreign waters, for the latter are stated in uncertain units, and it could only be determined in the special apparatus employed by the foreign scientists.

The figures given above as representing the radio-activity of the waters and natural gas must not be taken for the weights of the niton. They are actually the weights of radium which would produce these amounts of niton. Thus the figure 1.73 means that 1.73 mgrms. of radium would be in balance with the amount of niton in the water. This conception is a little difficult, and a few words of explanation are necessary.

Suppose 1 grm. of radium to be dissolved in water, say, as chloride or bromide. It is continually giving off niton; but at the same time, the niton is as continuously disappearing, owing to the formation of radium A, B, C, and D. There will arrive a time when the production of niton from the radium will have ceased to increase, because as it is produced it decays, and the rate of production is then equal to the rate of decay. The amount of niton will therefore increase up to a certain point; that point is when 0.6 of a cubic millimetre of niton has been produced. The weight of 1 cubic millimetre of niton is almost exactly 1/100th of a mgrm., hence 0.6 cubic millimetre weighs 6/1000ths of a mgrm. This is the weight of the niton which is equilibrium with 1 grm. of metallic radium. But we have 1.73 mgrms. of radium, in equilibrium with the niton in the King's Well. Hence as 1000 mgrms. : 1.73 mgrms. :: 0.006 mgrm. : 0.0000104 mgrm. That is, the weight of the niton in a million litres of the water of the King's Well is about 1/100,000 mgrm. But its effect is that of 1.73 mgrms. of radium in a million litres. The same reasoning applied to the gas would show that its effect is due to about 1/3000 of a mgrm. of niton in a million litres; or in the daily output, 5363 litres, about 1/600,000th of a mgrm. of niton, equal in effect to the gas in balance with 1/5th of a mgrm. of radium.

These figures appear to be ridiculously small; but it must be remembered that the effect of radium is due to radiations of exceeding intensity, and very penetrating; and at present, although very few observations have been made on chemical change induced by the action of radium and its products, we do know that considerable changes are produced under the action of quantities of radium comparable with the amounts given above.

*Use of the Waters and the Natural Gas.*—Experiments which I have made in conjunction with Dr. Stevenson in

the Medical School at University College, in which mice were fed with bread and cheese soaked in a solution of niton, and in which kittens were injected with a similar solution, as well as fed with it, have shown that the niton is got rid of chiefly by the lungs, and that in about three hours. After twelve hours all traces have disappeared. It may be that when a patient takes a bath, the skin absorbs some niton; and some undoubtedly enters the lungs, for it is continually being given off from the surface of the hot water. Assuming this to be the case, it may be asked whether there is any means of increasing the dose taken by each of these methods of absorption.

Considering first skin absorption, this might be greatly increased in the following way:—You already have a very pretty installation for giving "electric baths." But the current is an alternating one; it may and undoubtedly does produce electric stimulus; but the fact of the rapid reversal of the current prevents any concentration of niton on the skin. Now, niton in disintegrating is continuously discharging electrons, or in the older phraseology, losing negative electricity, and becoming positively charged. It follows that it will be attracted by a negatively charged body. If the patient in the electric bath were connected with the negative pole of a battery giving, say, 100 volts potential, or even more, and the other electrode were placed in the water, of course not in contact with the bather, the niton would rapidly reach the skin. It is, indeed, not unlikely that it would enter the system by so-called "ionisation," and in this way a considerable dose might be given. The apparatus would require the substitution of a continuous for an alternating current, and suitable measuring instruments, but this would entail no great expense. Naturally, any experimenting on these lines would require to be made with caution; I do not know of any attempts in such a direction. I suppose that such a bath as is in use may contain about a cubic metre of water; if that be so, then the amount of niton in the bath would be about the thousandth part of the figures given above. This amounts roughly to the thousandth of a mgrm.; and even if it were all absorbed, it could not, judging by the results of the experiments on kittens, prove a dangerous dose.

Coming next to the administration of much stronger doses, that is in your power. There is an ingenious spraying machine, constructed, I am informed, by Mr. Jones, chiefly used, I was told, for throat affections. This is fed with air, or with air and steam, carrying with it the natural water. Now, if the natural gas were used for this purpose, an agent nearly twenty times as potent would be available. I fancy that the spray produced by forcing the gas under pressure through the water could be employed directly against the skin. It occurs to one that that might prove efficacious in the treatment of local rheumatism. If, at the same time, the patient were insulated and connected with the negative pole of a battery, the chances of absorption would be greatly increased. There would be no difficulty in arranging such an apparatus. It might be possible to make the patient breathe the spray, for absorption by the lungs would no doubt be very rapid; but this, I think, should be tried with caution.

The total quantity of niton available in the gas from the King's Spring in twenty-four hours is the equivalent of about 0.17 of a mgrm. of radium. In a room 15 feet cube there would be little more than the thousandth of a mgrm. per cubic yard. I am afraid that ventilation would be defective were it arranged to allow the niton to accumulate in a room in which people would assemble to breathe it. It would appear to be preferable to administer it in the form of spray.

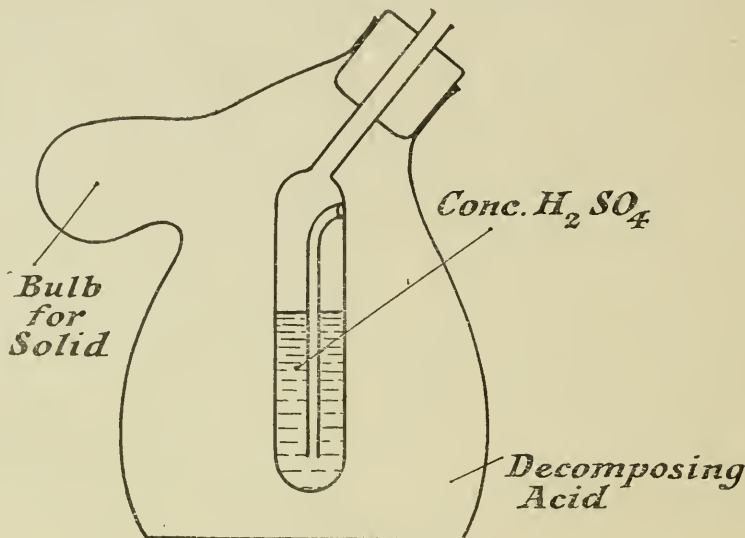
I am at present engaged in an exhaustive analysis of the residue from the waters of the King's Well. If the Committee desires, they are welcome to a copy of it, as soon as it is complete. But I thought it better to send this report as soon as possible, for it deals with the constituents of the water which have interest from the point of view of therapeutics.

## ESTIMATION OF CARBONIC ACID.

By H. M. ATKINSON.

A DISADVANTAGE of many of the very numerous CO<sub>2</sub> flasks now on the market is the necessity of sucking out the gas formed, or removal by other means after the decomposition of the carbonate. Again, unless the acid is previously saturated with CO<sub>2</sub> the amount of this retained by the acid is considerable if much acid be used; hence many operators heat or even boil after the action is over, with risk of loss of water vapour.

The form of flask I have lately been experimenting with is meant to avoid these difficulties. The side-bulb is for reception of the carbonate, the flask held upside down, and the solid put in by aid of a paper-cone. The flask (of total volume about 150 cc.) contains the acid, which can

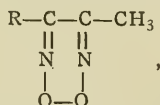


be in considerable quantity; this acid can be added from a bottle direct, or better from a pipette. Before corking and weighing I now fill the flask with CO<sub>2</sub>, by dropping into the acid some pieces (about 1 to 1.5 grms.) of marble; when these are dissolved the stopper with drying tube is put in, then weighed, and the acid cautiously allowed to act on the carbonate.

With concentrated H<sub>2</sub>SO<sub>4</sub> in the tube efficient drying takes place, and the flask, after a short time for cooling, is ready for weighing to get the loss in weight.

Municipal Technical Institute, Limerick.

**Constitution of Diisoeugenol.**—E. Puxeddu.—Light causes the polymerisation of isoeugenol to diisoeugenol, the yield being about 60 per cent of the theoretical quantity. Similar reactions occur with the ethyl and methyl ethers of isoeugenol. Eugenol and its ethers are not affected by light. Nitrous acid gives with ethyl isoeugenol a peroxide of formula—



where R = C<sub>6</sub>H<sub>3</sub>(OCH<sub>3</sub>)(OC<sub>2</sub>H<sub>5</sub>).—*Atti della Reale Accademia dei Lincei*, xxi., No. 1.

## THE DETERMINATION OF VANADIUM IN VANADIUM AND CHROME-VANADIUM STEELS.\*

By J. R. CAIN.

(Concluded from p. 127).

*The Method in Detail.*

DISSOLVE 2 to 4 grms. of steel in 40 to 60 cc. of 10 per cent (by volume) sulphuric acid, in a covered 300 cc. Erlenmeyer flask. Filter off the insoluble, wash two or three times with water, ignite, and fuse for a few minutes with acid potassium sulphate, adding the aqueous solution of the fusion to the main solution. If the steel will not dissolve readily in sulphuric acid, hydrochloric acid may be used, fusing the insoluble as before. (In this case

the carbonate precipitate must be dissolved in sulphuric acid, and the separation repeated in sulphate solution, for the precipitate first obtained contains enough chloride to give trouble if dissolved in sulphuric acid and directly electrolysed). Nearly neutralise the solution of the steel with saturated sodium carbonate solution. Then add finely pulverised cadmium carbonate in small portions at intervals of four or five minutes, boiling vigorously between times, keeping the flask well covered. A grm. or two of carbonate should remain at the end of the operation. About fifteen or twenty minutes' boiling always suffices. The time may be even shorter for vanadium steels containing little or no chromium. Allow the precipitate to settle and filter rapidly, so as to prevent oxidation and precipitation of iron on the filter (an 11 cm. S. and S. No. 589 white label filter is recommended). Wash the precipitate twice with hot water; no care need be taken to remove all of it from the flask. Dissolve the precipitate with the minimum of nearly boiling 10 per cent sulphuric acid, catching the filtrate in the flask. Boil to ensure solution of material adhering to the sides of the flask. Cool and nearly neutralise with ammonia; there should be no more free acid present than is necessary to prevent the iron from precipitating by hydrolysis when the solution is boiled. Pass a rapid current of hydrogen sulphide for a few minutes while the solution is boiling vigorously. Let the precipitate settle, filter it off, and wash two or three times with hot water. Concentrate the filtrate if necessary, and electrolyse

\* *Journal of Industrial and Engineering Chemistry*, iii., No. 7.



in a volume of 60 to 70 cc., using 5 to 6 ampères at 6 to 7 volts. The amount of mercury used in the special apparatus described below was about 200 grms. The solution is tested for iron by ferricyanide; usually when no iron test is obtained all the chromium is removed. However, should there be an unusually large amount of chromium relatively to the iron this might not happen. In this case the test should be made by removing 3 or 4 cc. of the solution, adding a few drops of hydrogen peroxide, and boiling for a few minutes after the brown colour, due to vanadium peroxide, disappears. If the solution now remains clear and colourless on adding ammonia, the electrolysis is ended. Acidify the test portion with sulphuric acid before returning it to the electrolysis apparatus. The simpler ferricyanide test usually answers for all purposes; the complications mentioned earlier, due to reduction of ferricyanide by quadrivalent vanadium, do not interfere in this case, inasmuch as there is no ferric iron to react with the resulting ferrocyanide. When the solution no longer gives a test for iron or chromium, remove it from the apparatus, and wash the mercury two or three times with 25 or 30 cc. of water while the current is still passing. Add 2 or 3 cc. of sulphuric acid (1:1 by volume), heat to 70° or 80° C., and add permanganate from a pipette until there is a strong pink colour. Run sulphur dioxide into the boiling solution for a few minutes; then pass a rapid current of carbon dioxide until the escaping steam gives no test for sulphur dioxide. Filter, preferably through asbestos or a Munroe crucible, cool the solution to 70° or 80° C., and titrate against N/50 potassium permanganate.

(NOTE.—The result will be slightly high if a paper filter is used. This is due to the hydrolysing and solvent action of the acid solution on the paper (even the best washed filter-paper). With alkaline solutions very serious errors may be incurred from ignorance of this fact).

For extreme accuracy repetition of the reduction and titration is recommended. The reduction may also be made by hydrogen sulphide, if desired. With special facilities a determination may be completed in one and a-half hours, or less.

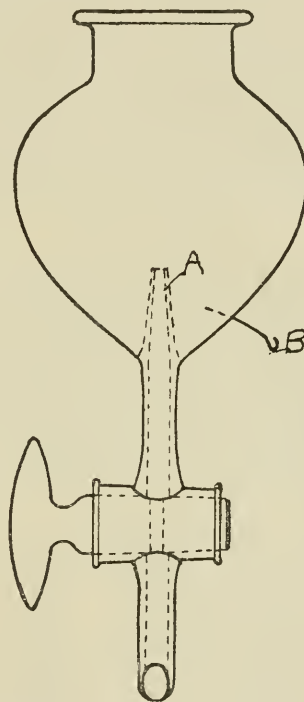
(NOTE.—Bleecker, *Met. and Chem. Eng.*, April, 1911, ix., 209), reduces vanadate solutions electrolytically, using a platinum dish as cathode. This method appears short and simple, and might be adopted in many cases. No work has been done here, however, along this line, and the exact conditions for complete reduction to the hypovanadate stage, and no further, would probably have to be determined. It is not safe to titrate directly the solution obtained by electrolysis as described without the preliminary permanganate oxidation followed by reduction and filtration as above; to do so usually gives irregular results).

#### Notes and Precautions.

Sufficient exclusion of air is secured by dissolving the steel in a flask kept well covered by a watch-glass. The fusion of the insoluble is absolutely necessary, as a large proportion of vanadium remains here; indeed, Nicolardot has proposed methods whereby, with complete exclusion of air, it is possible to secure practically all the vanadium in the insoluble portion when operating on certain classes of materials. This makes a quick and easy qualitative test for vanadium in steel, for as soon as the carbon is burned off the characteristic appearance of the fused vanadium pentoxide is very striking.

The treatment of the insoluble requires but a few minutes. The operations of solution, of cadmium precipitation, and of filtration must be done promptly, for a delay between solution and precipitation gives opportunity for oxidation of iron. This is to be avoided since it increases the amount of iron going into the carbonate precipitate, thereby prolonging the electrolysis, and also interfering with the complete precipitation of the vanadium and chromium. In this latter connection it seems that the particles of carbonate become rapidly coated with the

excessive precipitate of ferric hydroxide, and this interferes with their efficiency in neutralising the solution. The operations of filtering and washing must be particularly rapid; there is no difficulty here if the solution, after boiling, is allowed to stand a few minutes before filtering; the precipitate settles readily and is easily filtered. Two washings with hot water are sufficient. Sometimes a little difficulty is experienced in dissolving the precipitate completely from the filter; this is particularly true if the filtration and washing have not been done rapidly and promptly, giving opportunity for a difficultly soluble coating to form over the surface, due to oxidation and precipitation of iron. However, this trouble will never be serious if the operations are conducted as directed; moreover, even if this iron is not all removed from the filter it is never found to contain vanadium after two or three washings with the dilute acid. The advantage of a carbonate precipitant over an oxide precipitant is shown here, because the carbon dioxide evolved during the process of solution very effectually breaks up the difficultly soluble



surface layer, permitting the acid to get at the main body of the precipitate. On the other hand, when using zinc oxide it is often very difficult to dissolve the precipitate with dilute sulphuric acid. The hydrogen sulphide precipitation of the excess of cadmium is accomplished quickly; the solution should be nearly neutralised with ammonia; sodium hydroxide or carbonate should not be used, as in this case sodium would be driven into the mercury during electrolysis, not only prolonging this operation, but introducing other complications; if the degree of acidity is right and a rapid current of hydrogen sulphide is used, the solution being boiled vigorously while this is passing, the cadmium sulphide settles readily, and is easy to filter and wash. The solution after filtration can be transferred at once to the electrolytic apparatus, which may have any of the usual forms, such as the convenient small beakers with sealed-in platinum wires at the bottom, described by Smith (*"Electro-analysis,"* Fourth edition). If many determinations have to be made how

ever, the apparatus shown in the figure has been found very convenient.

The apparatus is a separatory funnel, shown in half size in accompanying figure with an inwardly projecting tube, A. The bore of the stopcock should preferably be as large as shown. A No. 18 platinum wire is sealed in at B. The apparatus is filled with mercury to within 1 or 2 mm. of the end of tube A, which itself is completely filled with mercury, and electrical connection is made to the negative terminal of the battery. The anode may have any of the usual rotating forms. The electrolysis vessel is conveniently supported by an iron ring clamped to the stand carrying the motor for rotating the anode. When electrolysis is completed the anode is brought as close as possible to the surface of the mercury without short-circuiting, and the electrolyte is allowed to run out by opening the stopcock. The washing is done very easily by a jet of water from a wash-bottle, leaving the stopcock open during the operation, the course of the washing being followed by the ammeter.

If a rotating anode is used the electrolysis is accomplished in fifteen or twenty minutes. The mercury may be used over and over again without purification; this is another advantage of removing the excess of precipitant before electrolysis, for the amount of foreign material going into it is thus reduced to a minimum. When a stock of mercury saturated with iron and chromium has accumulated it may be purified by the rapid method of Hillebrand (*Journ. Am. Chem. Soc.*, 1909, *xxi.*, 933). A fair degree of purification can be attained in a few minutes by shaking in a separatory funnel with concentrated hydrochloric acid.

#### Analytical Data.

Table I. gives some results that have been obtained on synthetic mixtures of chromium, vanadium, and iron. The vanadium was added from a stock solution of sodium vanadate which was carefully standardised by reducing several portions with sulphur dioxide and titrating against permanganate; the iron was from a sulphuric acid solution of a Bessemer steel with 0.1 per cent carbon, and the chromium from a roughly standardised chrome-alum solution. Precipitation by cadmium carbonate was made in the presence of 4 grms. of iron, one-half of the solution of the precipitate being used for electrolysis.

TABLE I.  
Vanadium.

| No.      | Present. | Found. | Error.  | Chromium. |
|----------|----------|--------|---------|-----------|
| 1 .. ..  | 0.0030   | 0.0030 | —       | 0.0286    |
| 2 .. ..  | 0.0030   | 0.0030 | —       | 0.0572    |
| 3 .. ..  | 0.0101   | 0.0102 | +0.0001 | 0.0358    |
| 4 .. ..  | 0.0117   | 0.0116 | -0.0001 | 0.0286    |
| 5 .. ..  | 0.0199   | 0.0204 | +0.0005 | 0.0572    |
| 6 .. ..  | 0.0376   | 0.0371 | -0.0005 | 0.3150    |
| 7 .. ..  | 0.0407   | 0.0410 | +0.0003 | 0.3150    |
| 8 (a) .. | 0.0010   | 0.0010 | —       | None      |

(a) In presence of 10 grms. of iron.

Determinations were made on the vanadium steel standard of this Bureau, first, from hydrochloric solution; second, from sulphuric solution. Duplicates gave 0.145 per cent vanadium and 0.142 per cent vanadium from the hydrochloric solution. To these there had been added 0.0750 gm. and 0.1064 gm. chromium respectively. In sulphuric solution, there was obtained 0.145 per cent. The mean of several very careful determinations by Bureau chemists, using different methods, was 0.143 per cent. On the new chrome-vanadium standard now in preparation the method gives 0.203 per cent and 0.203 per cent. The averaged complete analysis of the vanadium standard and of the chrome-vanadium standard (full data for the latter have not yet been received and the analysis given is not final) are shown in Table II.

TABLE II

| Standard. | Vanadium. | Chrome-vanadium. |
|-----------|-----------|------------------|
| C .. ..   | 0.350     | 0.377            |
| Si .. ..  | 0.303     | 0.113            |
| P .. ..   | 0.035     | 0.043            |
| S .. ..   | 0.027     | 0.029            |
| Mn .. ..  | 0.669     | 0.58             |
| V .. ..   | 0.15      | 0.197            |
| Cr .. ..  | 0.007     | 1.36             |
| Ni .. ..  | 0.009     | 0.15             |
| Cu .. ..  | 0.022     | 0.056            |
| Mo .. ..  | 0.006     | —                |

The results show that a satisfactory degree of accuracy is attainable; this may be increased even more, if desired, by using a larger sample of the steel, for there is no reason why the vanadium should not be concentrated from 10 grms. or more of steel, if desired. The minimum amount of vanadium here determined equivalent to 0.01 per cent in a steel (No. 8 of Table I.) shows how delicate the method is; the maximum amount (No. 7 of Table I.) shows the possibility of using cadmium precipitation, followed by electrolysis, for high vanadium products. The complete and quick precipitation of large amounts of chromium by cadmium carbonate is equally striking; a method for determining chromium in various kinds of steel, based upon these observations, is being worked out in this laboratory.

From what has been said of the effect of the presence of other substances when titrating hypovanadate solutions with permanganate it is evident that a method like this has distinct advantages in eliminating other metals. If the method is to be used for other steels than those for which it was devised, the effect of other metals must be considered. Such metals as copper and nickel would not interfere. The behaviour of molybdenum and tungsten in appreciable amounts has not been investigated, but molybdenum, if at all precipitated by cadmium carbonate, may be eliminated during the hydrogen sulphide precipitation of the excess of cadmium. Tungsten might be removed by evaporation of the cadmium precipitate with nitric acid, followed by filtration. After conversion of the nitrate to a sulphate solution electrolysis could follow as above described. Titanium would probably be precipitated by the cadmium, and remain with the vanadium through the electrolysis; however, it would not be reduced by sulphur dioxide nor hydrogen sulphide. These points will be investigated as opportunity permits.

#### Summary.

1. Various errors in the usual methods for determining vanadium in steel are pointed out, and in a few cases methods for correcting or eliminating these are indicated.
2. A short and accurate method for determining vanadium in vanadium and chrome-vanadium steels is discussed and described.

The writer is indebted to Dr. Hillebrand for many helpful suggestions during the course of this investigation.

**Double Carbonates of Calcium.**—M. Barre.—From a concentrated solution of sodium carbonate and precipitated calcium carbonate orthorhombic crystals are deposited, after boiling for some hours. The formula of the crystals is  $\text{CaCO}_3 \cdot \text{Na}_2\text{CO}_3 \cdot 2\text{H}_2\text{O}$ . They are slowly decomposed by water in the cold. The concentration of the sodium carbonate solutions has to exceed certain definite values which increase slightly with the temperature.  $16^\circ$  is the lowest temperature at which the double carbonate is formed. By a similar method the double carbonate  $\text{CaCO}_3 \cdot \text{K}_2\text{CO}_3$  can be obtained; it is decomposed by water, and is stable only in presence of potassium carbonate solution. Strontium and barium carbonates give no double salts.—*Comptes Rendus*, *cliv.*, No. 5.



# PROCEEDINGS OF SOCIETIES.

## ROYAL SOCIETY.

Ordinary Meeting. March 7th, 1912.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"Devitrification of Silica Glass." By Sir WILLIAM CROOKES, O.M., For.Sec.R.S. (Will be inserted in full).

"The Volatility of Metals of the Platinum Group." By Sir WILLIAM CROOKES, O.M., For.Sec.R.S. (Will be inserted in full).

"Critical Study of Spectral Series. Part II. The Principal and Sharp Sequences and the Atomic Volume Term." By Prof. W. M. HICKS, Sc.D., F.S.S.

This is a sequel to a paper on the same subject published in the *Philosophical Transactions* (1910, vol. ccx.). The sequences which give the principal and the sharp series are discussed as they occur in the second and third groups of the Periodic Table of the elements, and it is found that in opposition to the rule in the alkalis the P-series is based on the s-sequence and the S-series on the p-sequence. Additional evidence is afforded to show that these sequences depend on atomic volumes of elements in quite definite way.

An attempt is made to allot the S and D series of europium and of radium. The spectrum of Eu affords special evidence that the element fills the gap between Cd and Hg, and from the series formulæ of both elements regarded as functions of their atomic volumes probable values of their densities are obtained, viz., 12.58 for Eu, and either 5.10 or 6.12 for Ra.

Further, the result obtained in Part I., that if the denominator of the p-sequence be thrown into the form  $m + 1 - W(1 - im^{-1}) + \mu - am^{-1}$  the ratio  $a/\mu$  is a constant (0.21520 with uncertainty in the last two digits), is confirmed for elements of second and third groups. A comparison of denominators of corresponding orders of P-series, and of these with those of S-series, gives relations which can be used as tests for their proper allocation in doubtful cases. In consequence slight modifications are suggested in Paschen's lists of upper lines of HgP and CaP.

Two appendices are added, one dealing with S and D series of Eu and Ra, the other giving lists of S and P series lines treated of, with some historical notes.

"An Optical Load-extension Indicator, together with some Diagrams obtained therewith." By Prof. W. E. DALBY.

The paper describes a new instrument by means of which automatic records of load-extension diagrams can be obtained with precision, the records being free from errors due to inertia, pencil-friction, and to any strains caused by the yielding of the testing machine in which the specimen is being tested. The specimen to be tested is placed in series with a weigh-bar, so that the load is applied equally to both weigh-bar and specimen.

The proportions of the specimen are so arranged that the load on the weigh-bar never exceeds or even approaches the elastic limit of the material of which it is made, whilst the load on the specimen may increase to the breaking-load.

A small light mirror mounted on an axis is connected with the weigh-bar so that it tilts proportionately to the extension of the weigh-bar, and is therefore proportionate to the load on the weigh-bar and measures the load acting on the specimen. A second mirror whose axis is at right angles to the first is connected mechanically to the specimen, so that, as the specimen extends, the mirror receives the angular motion in proportion to the extension between assigned gauge points.

A beam of light from a source within the instrument is directed upon the first mirror and reflected from it to the second mirror, from which it is again reflected and

focussed on a ground-glass screen, which can be replaced when desired by a photographic plate.

There is no connection between the instrument and any part of the framework of the machine, the former being attached to the weigh-bar only.

To take a diagram all that is necessary is to place the instrument in position and on the weigh-bar, apply a load to the specimen by any suitable means, and the diagram is obtained automatically. Examples of diagrams are given together with methods for calibrating them.

"Transmission of Cathode Rays through Matter." By R. WHIDDINGTON.

It has been found experimentally that a cathode ray moving with velocity  $v_0$  can possess, after traversing a thickness  $x$  of material, a velocity  $v_x$  given by the relation  $v_0^4 - v_x^4 = ax$ ; where  $a$  is a constant depending on the nature of the material.

This constant  $a$  has been measured for aluminium, gold, and air at 760 mm. and 15°C., with the following results:—

|     |         |                       |
|-----|---------|-----------------------|
| Al  | .. .. . | $7.32 \times 10^{+2}$ |
| Au  | .. .. . | $2.54 \times 10^{+3}$ |
| Air | .. .. . | $2.0 \times 10^{+0}$  |

There seems to be no simple law connecting  $a$  with density or atomic weight of absorbing material.

"Velocity of the Secondary Cathode Particles Ejected by the Characteristic Röntgen Rays." By R. WHIDDINGTON.

Application of the results of the preceding paper to the experimental investigations of Beatty into the absorption of cathode particles in air leads to the conclusion that the fastest of the secondary cathode particles ejected from a plate by Röntgen rays characteristic of the element of atomic weight  $w$  possess a speed equal to  $k'w$ , where  $k'$  is a constant nearly equal to 10<sup>8</sup>.

"Potential Effect in Selenium." By E. E. FOURNIER D'ALBE.

A new type of selenium bridge (or "selenium cell") was constructed by coating a plate of unglazed porcelain of high insulating power with graphite, and dividing the surface into two conducting portions by cutting, with a diamond, a to-and-fro line through the graphite. The plate was then coated with selenium and sensitised. The bridges so constructed showed no polarisation, and were well adapted to the study of the "potential effect," or the change of resistance with the voltage applied. The resistance was found in each case to fulfil the relation  $R = R_1(1 - F \log V)$ , where  $R_1$  is the resistance for 1 volt,  $V$  is the voltage, and  $F$  a constant for any given bridge under constant conditions as to illumination, temperature, and fatigue.  $F$  varies from 0.1 to 0.5. The relation holds down to 1 volt and up to a point (100 to 200 volts) at which Joulean heating becomes perceptible. It also holds when the bridge is immersed in liquid air. A detailed investigation confirmed the opinion of others that the potential effect cannot be ascribed to heat.

## CHEMICAL SOCIETY.

Ordinary Meeting, March 7th, 1912.

Prof. J. NORMAN COLLIE, Ph.D., F.R.S., Vice-President, in the Chair.

MESSRS. H. J. Backer, John C. Withers, George A. Stokes, Rowland H. Ellis, B. C. Smith, and Thomas A. Brunjes were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Daniel Arkell, B.Sc., Oratory School, Birmingham; Evelyn Ashley Cooper, B.Sc., Arborfield, Woodcote Valley Road, Purley, Surrey; Frederick Charles Eastick, B.A., The Drive, South Woodford; John Burke Farlie, jun., 54, Wellington Road, Old Charlton, S.E.; Oliver Richard Howells, B.Sc., Bracondale School, Norwich; James O'Mara, B.A., Dunlica, College Road, Dulwich,

S.E.; John Rennie, Maisonne, Rufford Park, Yeadon, Leeds; Arthur Thompson, Bryn Teg, Chetwynd Road, Wolverhampton.

A ballot for the election of Honorary and Foreign Members was held, and the following were subsequently declared duly elected:—Prof. Philippe A. Guye (Geneva), Dr. Thomas Burr Osborne (Newhaven, Conn.), Prof. Paul Walden (Riga), Prof. Richard Willstätter (Zürich).

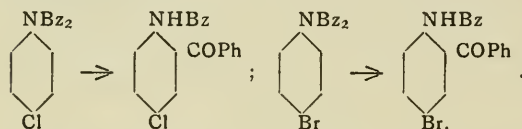
The names of the Fellows recommended by the Council for election as Officers and as Ordinary Members of Council for the year 1912 to 1913 were read from the Chair.

Of the following papers, those marked \* were read:—

\*37. "Isomeric Change of Halogen-substituted Diacylanilides into Acylaminoketones." By ANDREA ANGEL.

The isomeric change of diacvanilides into derivatives of *o*-aminobenzophenone, which has been shown to occur (*Trans.*, 1904, lxxv., 386) under the influence of heat and a catalyst when an alkyl group is present in the para-position with respect to the nitrogen atom, has been found to take place in a similar manner if negative para-substituents such as chlorine or bromine are present in the acylated aniline.

Dibenzoyl-*p*-chloroaniline and dibenzoyl-*p*-bromoaniline undergo rearrangement into 5-chloro-*o*-benzoylamino-benzophenone and 5-bromo-*o*-benzoylamino-benzophenone respectively, thus:—



These are pale yellow crystalline substances, melting at 108° and 122° respectively, which are with some difficulty hydrolysed to the corresponding aminohalogenbenzophenones.

5-Bromo-*o*-aminobenzophenone (m. p. 111°) resembles the chloro-compound very closely (*loc. cit.*, p. 344). It crystallises from dilute alcohol in bright yellow needles, and is somewhat volatile in steam. It is a weak base, forming crystalline salts with acids, which, however, are so readily hydrolysed that they turn yellow in moist air.

\*38. "Studies in the Camphane Series. Part XXXII. Stereoisomeric Modifications of isoNitroso-epicamphor, the Third and Fourth Monoximes of Camphorquinone." By MARTIN ONSLOW FORSTER and HANS SPINNER.

Although arylimino-derivatives of camphor, when heated with hydroxylamine hydrochloride and sodium acetate, yield either ordinary isonitrosocamphor or the dioxime of camphorquinone (*Trans.*, 1909, xcv., 942), there are produced from phenyliminocamphor in presence of alkali two

isomeric oximes. The  $\alpha$ -oxime,  $C_8H_{14}$  ,

crystallises from alcohol in massive transparent sulphur-yellow prisms, melting at 112°, and has  $[\alpha]_D^{25} 335.4^\circ$ . The  $\beta$ -oxime separates less readily from alcohol, but does not dissolve so freely as the isomeride in benzene, chloroform, or petroleum; it crystallises in very pale brown needles melting at 172°, and has  $[\alpha]_D^{25} 304.4^\circ$ . This modification is transformed into the isomeride when heated above the melting-point.

isoNitroso-epicamphor,  $C_8H_{14}$  , as obtained by

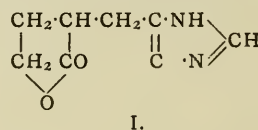
hydrolysing the  $\alpha$ -oxime of phenyliminocamphor with dilute hydrochloric acid, melts at 137°, and has  $[\alpha]_D^{25} -179.4^\circ$ . If the fused substance is heated further, it becomes semi-solid owing to transformation into a more stable isomeride, which is conveniently produced by boiling an aqueous solution of the unstable one; this form of isoNitroso-epicamphor crystallises from water in long lustrous

flat needles, melting at 170° and has  $[\alpha]_D^{25} -200.1^\circ$ . The two substances differ markedly as regards their solubility in petroleum, and they form distinct benzoyl derivatives; both develop with alkali hydroxide the yellow coloration characteristic of isonitroso ketones, and the diluted solution yields with ferrous sulphate a bluish violet precipitate resembling that given by isonitrosocamphor. Phenylhydrazine leads to an oxime of camphorquinonephenylhydrazone, whilst hydroxylamine gives rise to a dioxime of camphorquinone. Hence it seems clear that the new isonitroso-ketones have to epicamphor (Lankshear and Perkin, *Proc.*, 1911, xxvii., 166) the relationship borne by the two modifications of isonitrosocamphor towards camphor itself.

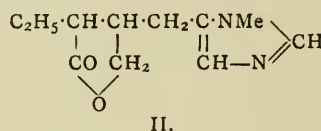
The production of isonitroso-epicamphor in two forms therefore completes the series of oximes theoretically obtainable from camphorquinone; four dioximes and four monoximes are now known.

\*39. "The Synthesis of Glyoxaline Derivatives Allied to Pilocarpine." By FRANK LEE P. MAN.

The lactone of  $\alpha$ -(3-hydroxyethyl)- $\beta$ -glyoxaline-4(or 5)-propionic acid (I.) which has certain constitutional features in common with pilocarpine (II.), has been prepared by hydrolysing ethyl 4(or 5)-glyoxalinemethyl- $\gamma$ -phenoxyethylmalonate, a product obtained by the action of 4(or 5)-chloromethylglyoxaline on ethyl  $\gamma$ -phenoxyethylmalonate:



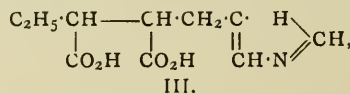
I.



II.

Neither this base nor an N-methyl derivative has any pronounced physiological action.

$\alpha$ -4(or 5)-Glyoxalinemethyl-3-ethylsuccinic acid (III.),—



III.

a compound containing the skeleton of pilocarpine, has been prepared by condensing 4(or 5)-chloromethylglyoxaline with ethyl  $\alpha$ -cyano- $\beta$ -ethylsuccinate, and hydrolysing the resulting ethyl 4(or 5)-glyoxalinemethyl- $\alpha$ -cyano- $\beta$ -ethylsuccinate. Its ethyl ester proved to be physiologically inactive. The preparation of 4(or 5)-glyoxalineformaldehyde,  $C_3N_3N_2.CHO$ , was also mentioned, and a description given of the free base, 4(or 5)-3-aminoethylglyoxaline.

\*40. "Calcium Nitrate. Part I. The Two-component System: Calcium Nitrate, Water. Part II. The Three-component System: Calcium Nitrate, Nitric Acid, Water at 25°." By HENRY BASSETT, jun., and HUGH STOTT TAYLOR.

The solubility of calcium nitrate in water has been studied between the temperatures of  $-28.7^\circ$  (the cryohydric temperature) and  $151^\circ$  (the boiling-point of the saturated solution). There are only three hydrates of calcium nitrate, namely,  $Ca(NO_3)_2.4H_2O$ ,  $Ca(NO_3)_2.3H_2O$ , and  $Ca(NO_3)_2.2H_2O$ , each of which is stable in contact with its saturated solution over a definite range of temperature. The tetra- and tri-hydrates have true melting-points.

The solubility of calcium nitrate increases rapidly with rise of temperature throughout the range of existence of the several hydrates, but at  $51^\circ$ , where the anhydrous  $Ca(NO_3)_2$  becomes the stable solid phase, the solubility

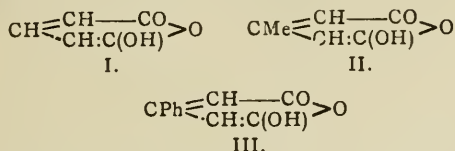


reaches a value which hardly changes with further rise of temperature.

The addition of nitric acid lowers the solubility of calcium nitrate, and at the same time promotes dehydration. Solubility determinations have been made at 25° between the limits of nitric acid concentration of 0 and 98 per cent. In contact with pure water and dilute nitric acid solutions,  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  is the stable solid phase, whilst the anhydrous  $\text{Ca}(\text{NO}_3)_2$  is alone stable in presence of the most concentrated acid solutions. Between these two extremes, however, there are well marked intermediate regions, where the stable solid phases are  $\text{Ca}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  and  $\text{Ca}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$  respectively.

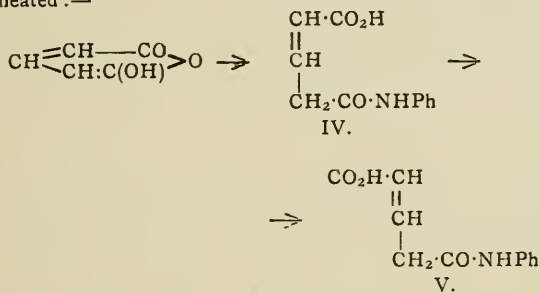
41. "The Chemistry of the Glutaconic Acids. Part III. Glutaconic Acid and its  $\beta$ -Alkyl Derivatives." By NORMAN BLAND and JOCELYN FIELD THORPE.

Glutaconic acid,  $\beta$ -methylglutaconic acid, and  $\beta$ -phenylglutaconic acid readily yield hydroxy-anhydrides of the formulæ I., II., and III. respectively:—

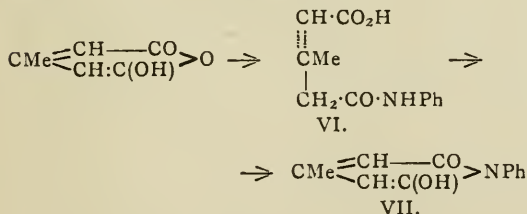


These compounds are monobasic acids, and give intense colorations with ferric chloride.

Glutaconic acid behaves towards aniline in the same manner as its  $\alpha$ -mono-substituted derivatives, and the *cis*-semianilide prepared from the hydroxy-anhydride and aniline (IV.) passes into the *trans*-semianilide (V.) when heated:—



The hydroxy-anhydrides from the  $\beta$ -substituted acids yields, on the other hand, semianilides (VI.), which pass into hydroxy-anils (VII.) when heated:—



The hydroxy-anils behave on titration as monobasic acids, but their salts are stable, and do not regenerate the salts of the semianilide when heated. It is evident that the attachment of an alkyl group to the  $\beta$ -carbon atom of glutaconic acid confers increased stability on those forms of the derivatives of the acids which have the mobile hydrogen outside the three-carbon system.

42. "Asymmetric Quinquevalent Nitrogen Compounds of Simple Molecular Constitution." By WILLIAM JACKSON POPE and JOHN READ.

In 1891 Le Bel described the preparation of methyl-ethylpropylisobutylammonium salts, and the manner in which, by the action of *Penicillium glaucum* on a solution of the corresponding chloride, he obtained a solution which exhibited a small rotatory power; from this observation Le Bel concluded that he had succeeded in obtaining optical activity which could be associated with the presence of an asymmetric quinquevalent nitrogen atom.

In 1899 Marckwald prepared salts of the above named base by the interaction of methylpropylisobutylamine and ethyl iodide, and, since he obtained no optical activity by the action of the organism as described by Le Bel, concluded that the latter author's observations were not correct. In a reply to Marckwald, Le Bel attributed the failure to confirm his observations to the production of a different quaternary ammonium iodide by Marckwald's process and his own, which consisted in causing ethylpropylisobutylamine to combine with methyl iodide.

The authors have prepared ethylpropylisobutylamine in a state of purity, and have found that it combines with methyl iodide, yielding a quaternary ammonium iodide identical with that obtained by the alternative method used by Marckwald. They find that the behaviour of ethylpropylisobutylamine towards methyl iodide is quite unlike that described by Le Bel.

It is consequently concluded that Le Bel did not succeed in preparing methylethylpropylisobutylammonium iodide, and that he did not obtain a substance of which the optical activity could be associated with the presence of an asymmetric quinquevalent nitrogen atom.

43. "The Interaction of Phosphorus and Potassium Hydroxide Solution." By MANINDRA NATH BANERJEE.

An explanation was given, by means of a series of equations, of the mechanism of the reaction between phosphorus and potassium hydroxide solution.

44. "The Triazo-group. Part XX. Azoimides of the Propane Series." By MARTIN ONSLOW FORSTER and JOHN CHARLES WITHERS.

By methods, the principles of which are familiar,  $\gamma$ -triazopropylamine was prepared along with  $\beta$ -triazopropylamine, which it greatly exceeds in stability, resembling  $\beta$ -triazoeethylamine.  $\alpha$ -Bistriazoisopropyl alcohol and  $\alpha$ -bistriazopropyl alcohol were described, together with the respective bistriazoethylpropanes; from the former of these  $\alpha$ -bistriazopropylene has been obtained.

45. "Viscosity and Association. Part II. The Viscosity of Geometrical Isomerides." By FERDINAND BERNARD THOLE.

The author has determined the viscosity of a large number of geometrical isomerides, typical members of the ethylenic compounds, the oximes and the phenylhydrazones being examined.

From the results certain general rules have been drawn, by help of which it has been possible to confirm the formulæ for the camphorquinonephenylhydrazones suggested by Forster and Zimmerlie (*Trans.*, 1911, xcix., 478), and to assign formulæ to the acetaldehydephenylhydrazones described by Lockemann and Liesche (*Ann.*, 1905, xxxiv., 214).

(To be continued).

Chemical Society.—At the Annual General Meeting, Thursday, March 28th, 1912, at 4.30 p.m., Prof. Percy F. Frankland, LL.D., F.R.S., will deliver his Presidential Address, entitled "Some Stereochemical Problems."

Imperial College of Science.—Dr. H. Brereton Baker, F.R.S., Lee's Reader in Chemistry in the University of Oxford, has been appointed to succeed Sir Edward Thorpe, F.R.S., as Professor of Chemistry in the Imperial College of Science and Technology, South Kensington.

## NOTICES OF BOOKS.

*The Chemistry of the Radio-elements.* By FREDERICK SODDY, F.R.S. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1911. (2s. 6d. net).

THIS monograph contains a complete *résumé* of our knowledge of the radio-active elements, regarded from the chemical point of view, and is a welcome addition to the series of monographs on inorganic and physical chemistry to which it belongs. It opens with a general description of radio-activity which every student of chemistry would do well to read. Radio-active equilibrium, periods of life, and radio-active constants are discussed in outline, and the classification and nomenclature of the radio-active elements are explained. The radio-active elements are then treated in turn. The important constants of each element are tabulated, such as the period of average life, the nature of the radiation, and the range of the rays, and the disintegration products are shown by schemes and tables. All references to the literature of the subject are given at the end of the monograph; the treatment is systematic in the extreme, and the book is one which any student who has a fair general knowledge of inorganic chemistry would read with ease and interest.

*Modern Microscopy.* By M. I. CROSS and MARTIN J. COLE. Fourth Edition. London: Baillière, Tindall, and Cox. 1912. (6s. net).

STUDENTS of the biological sciences will find this book a valuable help to them in their microscopical work, and amateurs who are interested in the study of scientific subjects could have no better handbook for their guide. It is intended more particularly for students and beginners, and discusses the purchase of a microscope, giving hints about the most useful instrument for various classes of work, the use of the microscope itself, and its accessory apparatus, and section-cutting, staining, and mounting. Some theoretical discussions are included, and are always very lucid and concise; thus many students of chemistry would find that the reading of the account of the polarisation of light would clear away much of the haziness of their ideas on the subject. A new third part has been added to the fourth edition. This contains articles, written by specialists, on many subjects which provide fascinating study for the amateur microscopist. Thus an "Introduction to the Use of the Petrological Microscope" has been contributed by Mr. F. J. Cheshire, F.R.M.S., and articles on the "Foraminifera and Rotifera" are reproduced from *Knowledge*, while the editor of that periodical writes an interesting account of the microscope and Nature study.

*Food and Drugs.* By ERNEST J. PARRY, B.Sc. (Lond.), F.I.C., F.C.S. Vol. I. and II. London: Scott, Greenwood, and Son. 1911. (21s. and 7s. 6d. net).

THE analysis of foods and drugs is treated in this book both from the chemical and legal points of view. In the first volume methods of analysis of articles of food and drugs are discussed in detail, and it could well be used as a practical laboratory guide. As a rule only reliable and commonly used processes are treated, and many tables of results are included. Some microscopic methods of investigation are described, and the author is well abreast of the times as regards modern processes and modifications, but spectroscopical work might with advantage have been given rather fuller treatment. The Essential Oils of the British Pharmacopœia are included in the section on Drugs. In the second volume the Sale of Food and Drugs Acts of 1875, 1879, and 1899, the Margarine Act of 1887, and the Butter and Margarine Act of 1907 are reproduced in full with some discussions of important cases which have arisen, and of the various rulings which have been given.

*Analytical Chemistry.* By F. P. TREADWELL, Ph.D. Authorised Translation from the German by WILLIAM T. HALL, S.B. Vol. II. *Quantitative Analysis.* Third Edition. New York: John Wiley and Sons. London: Chapman and Hall, Ltd. 1911.

THE third edition of this widely known and much appreciated work has been compared with the fifth German edition, which has recently appeared, and the necessary alterations and additions have been made. The second volume contains a comprehensive treatment of methods of gravimetric and volumetric analysis and gas analysis, and no quantitative processes which have been described in chemical literature, and which have been found accurate and convenient, are passed over. The translator has made some slight alterations with the object of making the book more useful to English-speaking students, who will find it an excellent reference book for their laboratory work.

*Die Darstellung von Bisulfiten und Sulphiten.* ("The Preparation of Bisulphites and Sulphites"). By Dr. Ing. E. SCHUTZ. Halle-a. S.: Wilhelm Knapp. 1911. (2.80 Mk.).

ALTHOUGH many processes for the preparation of salts of sulphurous acid are described in patent and current literature, the author of this book claims that he is the first to collect and give a complete survey of them in the form of a monograph. He includes all the most widely used of the salts of sulphurous acid, and gives the results of his own practical experience with regard to some disputed or doubtful points. The first chapter contains a detailed account of the manufacture of sulphur dioxide; firstly, from sulphur, and, secondly, from ores containing sulphur, with plans of the apparatus which is employed on a large scale. The purification of the gas is next discussed, and the special difficulties encountered in the process are fully treated. In the third chapter the preparation of all the most important salts is described in detail, with diagrams and illustrations, and finally some account is given of the various uses to which the sulphites and bisulphites are put.

*Atlas Typischer Spektren.* By Von Hofrat Dr. E. M. EDER und Prof. E. VALENTA. With 53 plates, including 643 spectra.

THE above Atlas is very complete, and includes reproductions of photographed spectra produced by glass and quartz trains, and also by a grating spectrograph. Flame, arc, and spark spectra are given between wave-lengths  $\lambda$  7000 and  $\lambda$  1850. Tables of measurements of the principal lines are given in Angstrom units to two places of decimals, and may be taken as accurate; the wave-lengths of the prominent lines are also engraved upon the plates. The preparation and reproduction of such a large number of spectra represents an immense amount of labour and expense, and it is to be regretted that they have not been produced upon a larger scale. In many cases the lines are so close together that only the most prominent can be resolved; this is particularly noticeable in the case of iron, a spectrum that cannot be too closely studied on account of the importance of its alloys. There is another very serious drawback to the use of the plates, in the fact that little or no attempt has apparently been made to obtain pure materials. In several instances a spectrum is given as that of an elementary substance, showing a mass of lines which upon closer inspection turn out to be almost all due to impurities; this renders the spectra quite useless for any lines that do not happen to be marked. Considering the ease with which many metals can be obtained in a state of purity, the elaboration and reproduction of spectra with impurities that actually mask those of the element it is supposed to represent, is unaccountable. Work of this kind shows the need of co-operation of the chemist with the physicist. At the same time we must congratulate Messrs. Eder and Valenta upon having produced the most advanced Atlas of spectra yet issued, and which must speedily find a place in every spectroscopic laboratory.



## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless other is expressed.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. cliv., No. 5, January 29, 1912.

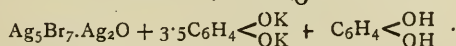
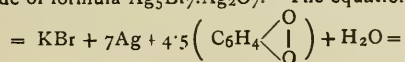
**Constitution of Chrysophanic Acid.**—E. Léger.—Tetranitrochrysophanic acid, when subjected to the action of nitric acid, gives 2.4.6-trinitro-*m*-oxybenzoic acid. This shows that the constitution of tetranitrochrysophanic acid and that of aloëmodin are very similar, and that the NO<sub>2</sub> and OH groups occupy the same positions in them. Thus the formula for chrysophanic acid suggested by Fischer is confirmed. By the action of KOH chrysophanic acid is converted into symmetrical oxymetaphthalic acid, and this fact proves that chrysophanic acid is 1.8-dioxy-3-methylantraquinone.

No. 6, February 5, 1912.

**Symmetry of Spartein.**—Charles Moureu and Amand Valeur.—The action of methyl iodide on the iodohydrates of spartein and isosparteïn gives absolutely analogous results. This suggests that sparteïn is not symmetrical, and the action of methyl iodide cannot be a simple addition. The authors have directly proved that the two iodomethylates of sparteïn are stereoisomers.

**Rôle of Interatomic Electrons in Catalysis.**—Pierre Achalmé.—In order to explain the phenomena of catalysis it may be supposed that the molecules are formed of atoms bound to one another by negative electrons exterior to the atoms. These interatomic electrons are definite in number. Then catalytic actions are reactions in which the interatomic electrons have undergone either a decrease or increase in number, or else a disturbance of the equilibrium, which has brought about a rearrangement of the atoms in the molecule.

**Preparation and Properties of a Silver Oxybromide.**—A. Seyewetz.—When an aqueous solution of quinone in presence of potassium bromide acts in the cold on silver in a very finely divided state a new argentic compound is obtained. Its composition corresponds to that of an oxybromide of formula Ag<sub>5</sub>Br<sub>7</sub>.Ag<sub>2</sub>O<sub>7</sub>. The equation is—



The oxybromide is a reddish brown amorphous powder which may be crystallised from ammonia. It is insoluble in water and in nitric acid. It is reduced by a current of hydrogen, giving metallic silver. When heated to a red heat it yields silver bromide. Potassium iodide gives a corresponding oxyiodide.

**Copper Amalgam.**—A. Guntz and M. de Greift.—When copper is dissolved in mercury the final product varies with the mode of preparation. The solution obtained by heating the amalgam (dissolved copper) is unstable, and after about seven days is converted into the stable modification (dissolved amalgam). In the case of cadmium the two amalgams CdHg<sub>3</sub> and Cd<sub>2</sub>Hg<sub>5</sub> can exist in solution, separately or simultaneously.

**New  $\alpha$ -Indenic Derivatives.**—V. Grignard and Ch. Courtot.—When magnesium  $\alpha$ -bromindene acts on an ethereal solution of cyanogen bromide,  $\alpha$ -bromindene is formed, and magnesium bromocyanide. With cyanogen chloride the products are  $\alpha$ -indenic nitrile and magnesium bromochloride. The sodium derivative of indene gives analogous reactions, but the yields are very decidedly lower.

**Preparation of Aromatic Alcohols.**—G. Vavon.—Hydrogenation in the cold in presence of platinum black transforms the aromatic aldehydes into alcohols. The author has applied this method to a great number of aldehydes, and finds that it is quite general, and is convenient and quick. The same platinum black can be used for a great many experiments in succession, the alcohols are obtained in a very pure state, and the yields are excellent.

**Reduction of Amides and of Ether Salts of the Fatty Series by Metal-ammonium.**—E. Chablay.—The lower amides, acetamide, propionamide, &c., decolorise a solution of sodammonium at -50° giving a white precipitate, which is a mixture of the monosodium amide and the sodium alcohol. The equations are 3R.CO.NH<sub>2</sub> + 3NH<sub>3</sub>.Na = 3R.CO.NH.Na + 3NH<sub>3</sub> + 3H and R.CO.NH<sub>3</sub> + 3H + NH<sub>3</sub>.Na = R.CH<sub>2</sub>.ONa + 2NH<sub>3</sub>. NaNH<sub>3</sub> is also decolorised by an ether salt very rapidly at -50°, a sodium amide and a sodium alcohol being formed.

## MISCELLANEOUS.

**Order of Merit.**—The King has been graciously pleased to make the following appointment to the Order of Merit:—Prof. Sir JOSEPH JOHN THOMSON, D.Sc., F.R.S. This appointment makes the number in the Order of Merit 19, and the other eminent men of science in the Order are Lord Rayleigh (an original member, appointed on August 9th, 1902), Dr. Alfred Russel Wallace (November 9th, 1908), and Sir William Crookes (July 8th, 1910). Sir Joseph John Thomson is especially distinguished for his work in the constitution of matter, in which he has made original researches of the greatest importance. He was born near Manchester in 1856, and was educated at Owens College and Trinity, Cambridge. In 1880, the year when Sir Joseph Larmor was senior wrangler, he was second wrangler and second Smith's prizeman. He has been Cavendish Professor of Experimental Physics at Cambridge since 1884, and Professor of Physics at the Royal Institution since 1905. In 1906 he was awarded the Nobel Prize for Physics. He has published "A Treatise on the Motion of Vortex Rings," 1884; "The Application of Dynamics to Physics and Chemistry," 1886; "Discharge of Electricity through Gases," 1897; and other works embodying his researches in electricity and magnetism. Sir Joseph Thomson's scientific eminence has been recognised by his election to honorary membership of many Foreign Academies, by the award of medals of the Royal Society and the Smithsonian Institute, and by numerous honorary degrees.—*The Times*, March 16, 1912.

**Chemical Laboratory Fresenius, Wiesbaden, Germany.**—At the Autumn Vacations Course, 1911, held at the Laboratory Fresenius, 28 students took part, including 2 ladies. During the regular Winter term, 1911-12, 38 students were inscribed, including 3 ladies. The nationality of the students was as follows:—22 were from Germany, 3 from Russia, 2 from England, 2 from Holland, 2 from Brazil, 1 from Austria, 1 from Belgium, 1 from Switzerland, 1 from Luxemburg, 1 from France, 1 from Spain, and 1 from Greece. The Directors of the Institute, Geh. Regierungsrat Prof. Dr. H. Fresenius, Prof. Dr. W. Fresenius, Prof. Dr. E. Hintz, are assisted by four duly qualified lecturers and heads of departments. Besides these there is a staff of 30 assistant chemists and sub-assistants, including including 7 ladies. The next Summer term will commence on April 24th, 1912. During the Winter 1911-12, a number of scientific treatises originated from the Laboratory Fresenius; they were published in different chemical journals, especially in the *Zeitschrift für Analytische Chemie*, edited by the Directors. As special prints appeared "Chemische Untersuchung der

neuen Heilquelle zu Wiessee am Tegernsee" and "Chemische Untersuchung der Mineralquelle zu Fachingen," both by Prof. Dr. Ernst Hintz, Wiesbaden, C. W. Kreidel's "Verlag," 1911. Besides the scientific work a great number of chemical analyses were executed during the Winter half-year 1911-12 for commercial, mining, industrial, and agricultural purposes, also in the interest of Sanitary Boards, Criminal, and other States Departments.

Eighth International Congress of Applied Chemistry, Washington and New York, September 4 to 13, 1912.—The attention of those of our readers who propose attending this Congress is directed to the importance of observing the following dates:—

May 15, 1912. All who desire to take part in the Yellowstone Park Tour must have their notification in the hands of the American Committee.

June 1, 1912. Reservations on the SS. "Cleveland" and "Philadelphia" remaining unsold at this date to members of the Congress will be disposed of as the Executive Committee may decide.

June 15, 1912. All persons desiring to take part in any tour apart from the Yellowstone Park Tour must have their notification in the hands of the American Committee.

June 30, 1912. All papers that authors expect to have printed and distributed at the time of the Congress must be in the hands of the American Committee.

July 15, 1912. All memberships received after this date by the American Committee are accepted on the condition that delivery of printed reports cannot be *guaranteed* to such members.

## MEETINGS FOR THE WEEK.

MONDAY, 25th.—Royal Society of Arts, 8. (Cantor Lecture). "Materials and Methods of Decorative Painting," by Noel Heaton, B.Sc.

TUESDAY, 26th.—Royal Institution, 3. "Ancient Britain," by Thomas Rice Holmes, Litt.D.

— Royal Society of Arts, 4.30. "British North Borneo," by Leonard Lovegrove.

— Faraday Society, 8. "Dry Batteries—the Relation between the Incidence of the Discharge and the Relative Capacity of Cells of different Manufacture," by S. W. Melsom. "Contributions to the Knowledge of Liquid Mixtures," by R. B. Denison. "Electrolysis in Liquefied Sulphur Dioxide," by L. S. Bagster and B. D. Steele. "Elimination of Potential due to Liquid Contact," by A. C. Cumming. "Vapour-pressure of Concentrated Aqueous Solutions," by E. P. Perman and T. W. Price.

WEDNESDAY, 27th.—Royal Society of Arts, 8. "The Whaling Industry of To-day," by Theodore E. Salvesen.

THURSDAY, 28th.—Royal Institution, 3. "Sexual Dimorphism in Butterflies," by F. A. Dixey, F.R.S., &c.  
Chemical, 4.30. (Annual General Meeting). The President's Address, "Some Stereochemical Problems."

— Royal Society. "A Confusion Test for Colour Blindness," by Dr. G. J. Burch. "Systematic Position of the Spirochaetes," by C. Dobell. "Influence of Selection and Assortative Mating on the Ancestral and Fraternal Correlations of a Mendelian Population," by E. C. Snow. "The Human Electrocardiogram—a Preliminary Investigation of Young Male Adults, to form a Basis for Pathological Study," by T. Lewis and M. D. D. Gilder. "Production of Variation in the Physiological Activity of *B. coli* by the Use of Malachite Green," by C. Revis. "Notes on some Flagellate Infections found in certain Hemiptera in Uganda" and "Notes on certain Aspects of the Development of *T. gambiensi* in *Glossina palpalis*," by Muriel Robertson. "Antelope and their Relation to Trypanosomiasis," by Dr. H. L. Duke.

FRIDAY, 29th.—Royal Institution, 9. "Results of the Application of Positive Rays to the Study of Chemical Problems," by Prof. Sir J. J. Thomson.

SATURDAY, 30th.—Royal Institution, 3. "Molecular Physics," by Sir J. J. Thomson, F.R.S., &c.

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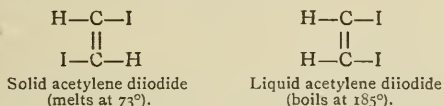
# THE CHEMICAL NEWS.

VOL. CV., No. 2731.

## THE SYNTHESIS OF FUMARIC AND MALEIC ACIDS FROM THE ACETYLENE DIIODIDES.

By EDWARD H. KEISER and LEROY McMASTER.

IN 1890 one of us (Keiser, *Am. Chem. Journ.*, xii., 99), by treating solid acetylene diiodide in alcoholic solution with potassium cyanide and caustic potash, succeeded in making fumaric acid. Subsequently in 1899 Keiser (*Am. Chem. Journ.*, xxi., 261) obtained for the first time a pure liquid isomer of the solid acetylene diiodide, and showed that these substances were geometrical isomers, and at that time expressed the view that the solid acetylene diiodide was to be regarded as the *trans* or fumaric form and the liquid geometrical isomer the *cis* or maleic form. Their configuration was represented thus:—



We have now established these formulæ by repeating and confirming the earlier work upon the synthesis of fumaric acid from the solid acetylene diiodide, and, in addition, we have transformed the liquid diiodide into maleic acid.

### Synthesis of Fumaric Acid.

*Experiment No. I.*—Solid acetylene diiodide (4.11 grms.) was dissolved in 150 cc. absolute alcohol, 3 grms. of powdered potassium cyanide added, and the mixture boiled on a water-bath under a reflux condenser for forty-seven hours. Three grms. of solid caustic potash were now added, and the heating continued for one and one-half hours, when ammonia was no longer given off. The solution was filtered and allowed to evaporate spontaneously. A mixture of crystals was obtained, some of which were needle-shaped. Qualitative tests showed the presence of iodide, cyanide, and fumarate in this mixture. The fumarate was then separated and purified as follows:—The crystals were dissolved in water, and silver nitrate added until a precipitate was no longer formed. The precipitate, consisting of silver fumarate and some silver iodide and cyanide, was digested with dilute ammonia, and the mixture filtered. The filtrate now contained the fumarate and some cyanide. Dilute nitric acid was now added in slight excess. This caused the cyanide to be precipitated, but held the fumarate in solution. After filtration the filtrate, containing the fumarate, was now made exactly neutral with ammonia. A white precipitate formed. This was collected upon a filter and again dissolved in dilute nitric acid, and precipitated by ammonia. The silver fumarate was then collected upon a hardened filter and dried at 100° for one and a-half days. The salt turned slightly brown, and when heated it deflagrated like gunpowder. Determinations of the percentage of silver gave the following results:—

|                                                                               |       |
|-------------------------------------------------------------------------------|-------|
| 0.1354 grm. of salt gave 0.1183 grm. AgCl.                                    |       |
| 0.2050 grm. of salt gave 0.1792 grm. AgCl.                                    |       |
| Calculated for C <sub>4</sub> H <sub>2</sub> O <sub>4</sub> Ag <sub>2</sub> . | I.    |
| Ag .. .. 65.43                                                                | 65.74 |
|                                                                               | II.   |
|                                                                               | 65.78 |

These determinations were made by dissolving the weighed amounts of fumarate in dilute nitric acid and adding hydrochloric acid in slight excess. The silver

chloride was filtered, dried, and weighed. The filtrate from the silver chloride, containing the free fumaric acid, was evaporated to dryness, when a white flaky residue was obtained. This was dried at 105°. It weighed, in the first analysis, 0.0428 grm. instead of 0.0476 grm., calculated. A small quantity of this residue was placed between watch-glasses and heated in an air-bath. At 200° it sublimed into the upper watch-glass. A sample of pure fumaric acid (Kahlbaum) acted likewise. Some small crystals of this synthetic fumaric acid were introduced into a melting-point capillary and heated beside a similar specimen of the pure fumaric acid in a sulphuric acid bath. At 200° each specimen sublimed to the upper cold part of the capillaries.

*Experiment No. 2.*—Ten grms. of solid acetylene diiodide and 7.5 grms. potassium cyanide were heated with alcohol for fifty hours on the water-bath under a reflux condenser. Eight grms. of caustic potash were then added and the boiling continued until ammonia was no longer given off. The hot alcoholic solution was poured off, and allowed to evaporate. The salt that separated was treated with dilute nitric acid and silver nitrate added. The precipitate was filtered off, and the filtrate was exactly neutralised with ammonia. The white precipitate of silver fumarate was re-dissolved and re-precipitated as in the first synthesis, and dried at 105–110°. It turned slightly brown on drying. A quantitative determination of silver gave this result:—

|                                                                               |        |
|-------------------------------------------------------------------------------|--------|
| 0.1734 grm. of salt gave 0.1516 grm. AgCl.                                    |        |
| Calculated for C <sub>4</sub> H <sub>2</sub> O <sub>4</sub> Ag <sub>2</sub> . | Found. |
| Ag .. .. 65.43                                                                | 65.80  |

The free fumaric acid was obtained by evaporating the filtrate from the silver chloride, as described above. It sublimed at 201° in the melting-point apparatus.

### Synthesis of Maleic Acid.

Liquid acetylene diiodide was prepared and purified by freezing as described by Keiser (*Am. Chem. Journ.*, xxi., 264). Ten grms. of the pure liquid diiodide and 7 grms. of potassium cyanide in absolute alcohol were boiled, under a reflux condenser, on the water-bath for fifty-three hours. The mixture turned pink, then dark brown, and finally black. A strong odour of isocyanide was noticed on opening the flask. Eight grms. of solid caustic potash were added, and the boiling continued for five hours, until the odour of ammonia had disappeared. The solution was filtered, a black residue remaining on the filter. This consisted chiefly of iodides and carbonaceous matter, but contained some maleate. The yellow filtrate was allowed to evaporate. The salts that separated were dissolved in water, and the water solution evaporated in a desiccator. The solid matter thus obtained was treated with just enough dilute hydrochloric acid to decompose the small amount of carbonate present, and then the solution was warmed to expel the gas. Barium hydroxide solution was now run in until the liquid was exactly neutral. On standing a short time a fine silky precipitate settled out. This precipitate was very similar in appearance and behaviour to barium maleate made in the same way from pure maleic acid (Kahlbaum). The synthetic barium maleate was filtered off and washed with cold water until the wash water gave no test for barium, chlorine, or iodine. The salt was then dried at 105° for eight hours. A determination of barium gave 52.26 per cent. As the calculated value for barium in anhydrous barium maleate, C<sub>4</sub>H<sub>2</sub>O<sub>4</sub>Ba, is 54.65 per cent, and in the salt with one molecule of water of crystallisation, C<sub>4</sub>H<sub>2</sub>O<sub>4</sub>Ba.H<sub>2</sub>O, is 51 per cent, it was evident that our salt was a mixture, or rather it was not dried sufficiently to completely convert it into the anhydrous salt. We found at this stage of the work that Vorländer (*Liebigs Ann. Chem.*, cclxxx., 192) stated that barium maleate does not lose water at 100° but begins to do so at 110°, and that the water is com-

pletely driven off at 130–135°. Another sample of the barium salt was dried at 110–125° for twenty-two hours. Determinations of barium now gave the following results:—

- I. 0.2434 grm. salt gave 0.2276 grm. BaSO<sub>4</sub>.  
 II. 0.1739 grm. salt gave 0.1610 grm. BaSO<sub>4</sub>.  
 III. 0.3502 grm. salt gave 0.3279 grm. BaSO<sub>4</sub>.

|            | Calculated for<br>C <sub>4</sub> H <sub>2</sub> O <sub>4</sub> Ba. | Found |       |       |
|------------|--------------------------------------------------------------------|-------|-------|-------|
|            |                                                                    | I.    | II.   | III.  |
| Ba .. .. . | 54.65                                                              | 54.98 | 54.45 | 55.04 |

A second synthesis of maleic acid was now made, with the same quantities of substances and the same method as before. The barium salt was prepared and purified as described above. It is to be noted that the fumaric acid is not precipitated by barium hydroxide under the conditions under which we made barium maleate. The barium maleate in this synthesis was dried at 135° for three days. The analysis gave the following results:—

0.2506 grm. salt gave 0.2340 grm. BaSO<sub>4</sub>.

|              | Calculated for C <sub>4</sub> H <sub>2</sub> O <sub>4</sub> Ba. | Found. |
|--------------|-----------------------------------------------------------------|--------|
| Ba . . . . . | 54.65                                                           | 54.9   |

Some of this barium maleate was tested for fumarate by dissolving it in hot water to which a little nitric acid had been added, then neutralising exactly with ammonia and adding silver nitrate. No precipitate of silver fumarate was obtained. Further, the free maleic acid from the barium salt, made in this synthesis, was prepared by dissolving the salt in hot water and adding sulphuric acid to the point of exact neutrality, then filtering off the barium sulphate and evaporating the filtrate. A melting-point determination of the white residue showed that it melted at 131°. Pure maleic acid (Kahlbaum) melts at 130°.

These experiments show conclusively that the solid acetylene diiodide can be converted into fumaric acid, and the liquid isomer into maleic acid. This makes it highly probable that these compounds have the configuration given above, namely, that the solid diiodide has the fumaric or *trans* form, and the liquid diiodide has the maleic or *cis* form.—*American Chemical Journal*, xlv., No. 5.

## IMINOSULPHIDES.

### PART I.—THE CONDENSATION OF THIOBENZAMIDE WITH BENZONITRILE.

By MOTOOKI MATSUI.

INFERRING from the fact that thiamide behaves as thioimino acid in many of its reactions, it was anticipated that it would combine with benzonitrile through the agency of hydrogen chloride, just as alcohols condense with nitriles under the same treatment, and thus would give rise to the iminosulphide of the constitution R·C:NH·S·NH·C·R', which has as yet received no mention in chemical literature; and this anticipation was proved to be correct. The present paper gives only a short account of experiments, carried out for the formation and examination of benziminosulphide, and forms a part of the research about the iminosulphides in general, undertaken by the author.

### EXPERIMENTAL PART.

#### *Benziminosulphide*, (C<sub>6</sub>H<sub>5</sub>·C:NH)<sub>2</sub>S.

The thio benzamide, prepared from benzonitrile and hydrogen sulphide and purified by the re-crystallisation from water, was mixed with benzonitrile in a molecular proportion, and the mixture was dissolved in absolute ether. Into the ethereal solution, kept cool with a freezing-mixture, dry hydrogen chloride gas was passed, whereupon the yellow solution gradually acquired a reddish tint.

When the solution was completely saturated with hydrogen chloride, the flask containing the solution was tightly stoppered with a cork, and left to stand over-night, after which a crop of orange needle crystals was found crystallising in the solution. The mother-liquor was decanted off, and the crystals were repeatedly washed with absolutely dry ether as promptly as possible, and placed in a vacuum desiccator for the ether to evaporate. From the crystals which are its hydrochloride benziminosulphide was isolated in a usual way, that is, by treating the hydrochloride with caustic potash, and, after saturating the alkaline solution with carbon dioxide, extracting it with ether. It may also be isolated by treating the hydrochloride with water, which completely decomposes it into its components. The ethereal solution thus obtained was evaporated, and the residue, after having been washed with warm water to remove thiobenzamide, was dissolved in benzene, and finally crystallised from the benzene solution on addition of petroleum ether. On analysis the following results were obtained:—

0.1170 grm. of the substance gave 0.2980 grm. CO<sub>2</sub>.  
 0.2086 grm. of the substance gave 20.7 cc. nitrogen at 23.5° and 753 mm.

|             | Calc. for (C <sub>6</sub> H <sub>5</sub> CNH) <sub>2</sub> S. | Found (per cent). |
|-------------|---------------------------------------------------------------|-------------------|
| Carbon ..   | 69.95                                                         | 69.49             |
| Nitrogen .. | 11.67                                                         | 12.43             |

Benziminosulphide crystallises in light reddish needles from its benzene solution on addition of petroleum ether, and melts at 71°. When crystallised from other solvents, such as alcohol or ether, it also forms needle crystals having, however, a more deep colour. It is very soluble in the ordinary organic solvents except petroleum ether, and produces a deep red solution. It dissolves both in acids and alkalis, forming an orange or yellow solution respectively. From the alkaline solution it is re-precipitated by carbon dioxide, and is partially extracted with ether. Its hydrochloride forms orange needles melting at 110–111°; it does not combine with platinum tetrachloride so as to produce the double salt. In an alcoholic solution the iminosulphide combines with picric acid, and yields a picrate crystallising in light reddish prismatic plates, and containing a molecule of alcohol. This alcohol of crystallisation is partly lost on exposure to the air, and completely driven out by heating at 80°, leaving the picrate as an amorphous yellow substance which melts at 114°. The hydrochloride and picrate were analysed with the following results:—

0.3282 grm. of the hydrochloride gave 0.2936 grm. AgCl.

|             | Calc. for (C <sub>6</sub> H <sub>5</sub> CNH) <sub>2</sub> S <sub>2</sub> HCl. | Found (per cent). |
|-------------|--------------------------------------------------------------------------------|-------------------|
| Chlorine .. | 22.65                                                                          | 22.12             |

- 0.2650 grm. of the picrate lost 0.0245 grm. on heating it for two hours at 80°.
- 0.1602 grm. of the picrate lost 0.0140 grm. on heating it for two hours at 80°.
- 0.2650 grm. of the picrate gave 0.2088 grm. acridine picrate.

|               | Calculated for<br>(C <sub>6</sub> H <sub>5</sub> CNH) <sub>2</sub> S <sub>2</sub> ·C <sub>6</sub> H <sub>2</sub> (NO <sub>2</sub> ) <sub>3</sub> OH. | Found (per cent). |      |       |
|---------------|------------------------------------------------------------------------------------------------------------------------------------------------------|-------------------|------|-------|
|               |                                                                                                                                                      | I.                | II.  | III.  |
| Alcohol ..    | 8.93                                                                                                                                                 | 9.25              | 9.36 | —     |
| Picric acid.. | 44.45                                                                                                                                                | —                 | —    | 44.19 |

The molecular weight of the iminosulphide was determined by the cryoscopic method, using benzene as the solvent. The results are as follows:—

|                           |        |
|---------------------------|--------|
| Substance ..              | 0.1630 |
| Solvent ..                | 15.601 |
| Dep. of freezing-point .. | 0.232° |
| Mol. weight—Calculated .. | 240    |
| Found ..                  | 225    |

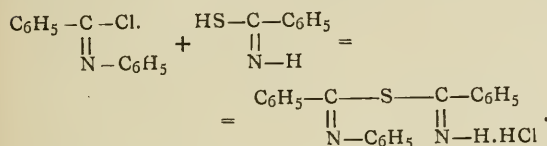
By the action of oxidising agents, such as nitric acid or



bromine, the substance partly changes into dibenzylazosulphime, which strongly resists the oxidising action even of fuming nitric acid, as was observed by Hofmann (*Ber.*, 1869, ii., 646). The clear solution, obtained by heating the iminosulphide with fuming nitric acid in a sealed tube for twelve hours at 180°, was observed still to contain some dibenzylazosulphime, which was precipitated from the solution by addition of water, and not more than 90 per cent of the total sulphur to have been oxidised into sulphuric acid. By warming the iminosulphide with a silver nitrate solution only about 70 per cent of the total sulphur was transformed into silver sulphide. Dibenzylazosulphime formed in this latter case was separated from silver sulphide by means of hot alcohol, and purified for its identification.

Benziminosulphide easily interacts upon acetyl chloride at ordinary temperature in a benzene solution, and yields an acetyl derivative crystallising in orange needles.

Iminosulphides are also expected to be formed from iminochlorides and thiamides, whose interaction may be represented by the following equation:—



Such reactions are now being studied by the author, and the results will be communicated before long.—*Memoirs of the College of Science and Engineering, Kyoto Imperial University*, ii., No. 13.

## VANADIUMISM.

DR. Walton Forest Dutton, of Carnegie, Pa., describes in the *Journal of the American Medical Association*, June 3, 1911, under the above name, a new industrial disease of interest to chemists, caused by the exposure to dust and fumes of the various vanadium compounds, especially vanadium trioxide.

Vanadiumism is a chronic intoxication, of which the symptoms are emaciation, an anæmia not altogether unlike chlorosis, a dry irritating paroxysmal cough, sometimes so intense that hæmorrhages result, irritation of the nose, throat, and eyes, gastro-intestinal involvement demonstrated by nausea and diarrhœa, followed by obstinate constipation. Albumin, casts, and blood are often present in the urine.

In the absence of grave, renal, blood, nervous, and lung involvement, the prognosis is good, but where there is active inflammation of the kidneys and lungs it is unfavourable. Dr. Dutton states that the prevention of vanadiumism is difficult in vanadium works, owing to the carelessness of employes and employers. Means to allay and carry off the dust and fumes should be employed constantly. Perfect ventilation and the use of respirators are imperative. The nasal and oral cavities should be thoroughly cleansed with some efficient alkaline spray, such as the ordinary Dobell solution, followed by a mentholated oil spray. The stomach should be washed out, and later the intestines freely evacuated with a saline laxative. The cough may be allayed by giving terpin hydrate  $\frac{1}{4}$  grain, heroin  $\frac{1}{4}$  grain, and creosote  $\frac{1}{4}$  minim, every two hours, with counter-irritations of iodine or mustard applications over the chest. The inhalation of stimulating vapours is salutary. Iron, calisaya, and strychnine will meet the needs of anæmic, nervous, and debilitated conditions. Cod-liver oil may be given with advantage. Active outdoor exercises are essential. Turkish, Russian, or cabinet baths may be given to aid elimination.—*Journal of Industrial and Engineering Chemistry*, iii., No. 7.

## THE DETERMINATION OF MANGANESE IN VANADIUM AND CHROME-VANADIUM STEELS.\*

By J. R. CAIN.

WATERS (*Met. Chem. Eng.*, 1911, ix., 244) has recently described a method for determining manganese in steels containing chromium and tungsten which eliminate the errors caused by using the bismuthate method on such steels, owing to the oxidation of some of the chromium by the bismuthate. The steel is dissolved in sulphuric acid and oxidised with nitric acid, the solution nearly neutralised, and the chromium and iron are precipitated with an emulsion of zinc oxide. An aliquot is filtered off, nitric acid added, and the manganese determined by the bismuthate method as usual. This method is very similar to one which the writer devised and has used for this class of materials. There is very little choice between the two, apparently, inasmuch as the time consumed, degree of accuracy, &c., is about the same in each case. However, the method to be described might give better results than that of Waters on high vanadium products, inasmuch as the vanadium in such cases might not always be completely precipitated by his method, and this would cause high results. Waters's method was tested as to this point with the Bureau of Standards chrome-vanadium standard, containing about 1.32 per cent of chromium and 0.20 per cent of vanadium, and no vanadium was found in the filtrate with the manganese. The percentage of manganese in the standard was found to be identical by the two methods.

It has already been shown (*Journ. Ind. and Eng. Chem.*, 1911, iii., 476) that large amounts of chromium and vanadium are completely precipitated from solutions of steel without co-precipitation of manganese, provided the iron is kept mainly in the ferrous condition while the solution is being boiled with the precipitant. To carry out the method for manganese, 1 or 2 grms. of steel are dissolved in sulphuric acid (10 per cent by volume), observing the precautions given in the last-quoted paper, and the chromium and vanadium precipitated by cadmium carbonate as described therein. To the filtrate from this precipitate add 25 cc. of concentrated nitric acid, and boil till free from fumes. Cool, oxidise with bismuthate, filter through asbestos, reduce with a measured excess of ferrous solution, and titrate as usual.

The method is quite rapid, and its use, or the use of similar methods which eliminate chromium and vanadium during the bismuthate oxidation, seems called for, inasmuch as the results of the co-operating analysts on the above standard were several hundredths of a per cent high where the bismuthate method was used. Further, the Ford-Williams method also gives high results, apparently due to occlusion of chromic acid. Some precipitates of manganese obtained by the Ford-Williams method from the chrome-vanadium standard were dissolved in sulphuric acid, neutralised with cadmium carbonate, and boiled. The precipitate showed appreciable amounts of chromium when dissolved in nitric acid and oxidised with potassium chlorate. A bismuthate determination of manganese in the filtrate gave a result agreeing with the determinations by the method of Waters and that of the writer.

Isomerism of the Ethers of Di-isoeugenol.—Ernesto Puxeddu.—The author has proved experimentally that the polymer of ethyleugenol and diethyl di-isoeugenol are two distinct substances. The chief differences between them are:—(i.) The former is slightly soluble in ether and in chloroform, while the second is very soluble; (ii.) the melting-point of the former is 140°, and of the latter 129–130°; (iii.) with bromine the former gives a product which is totally different from that furnished by the second.—*Atti della Reale Accademia dei Lincei*, xxi., No. 2.

\* Published by permission of the Director of the U.S. Bureau of Standards. From the *Journal of Industrial and Engineering Chemistry*, iii., No. 9.

# THE DETERMINATION OF GLIADIN OR ALCOHOL-SOLUBLE PROTEIN IN WHEAT FLOUR.

By RALPH HOAGLAND,

OSBORNE in his monograph, "The Proteins of the Wheat Kernel" (pub. by Carnegie Inst., 1907), states that the following proteins are present in the wheat kernel:—"Gliadin insoluble in neutral aqueous solutions, but distinguished from all others by its ready solubility in 70 per cent alcohol; glutinin, a protein having a similar elementary composition to gliadin, soluble in dilute acid and alkaline solutions, and yielding a wholly different proportion of decomposition products when boiled with strong acids; leucosin, an albumin-like protein, freely soluble in pure water, and coagulated by heating its solution to 50–60°C.; a globulin, similar in composition and properties to many globulins found in other seeds, and one or more proteoses which are present in very small quantity."

Osborne states that globulin, albumin, and proteose are the proteins found in the embryo of the wheat kernel, while the endosperm consists nearly entirely of gliadin and glutinin. The latter part of this statement of Osborne's is hardly correct, since wheat flour contains considerable proteid material—globulin, albumin, and proteose, soluble in dilute salt solution—usually amounting to 10 to 15 per cent of the total protein (see Chamberlain, *Bull.*, 90, p. 124, Bureau of Chem. U.S. Dept. of Agr.). However, the proteins of the wheat endosperm do consist very largely of gliadin and glutinin.

The quantitative separation of the proteins of wheat flour is very difficult and not possible of absolute accuracy, since no one protein is entirely insoluble in the solvent used to extract another protein. Thus while a 10 per cent sodium chloride solution will extract albumin, globulin, and proteoses, yet it will also extract some gliadin. Likewise, 70 per cent alcohol, while presumably extracting only gliadin, also extracts some albumin, globulin, &c. Chamberlain has done a large amount of work in the quantitative separation of proteins of wheat flour (see *Bull.* 81 and 90, Bureau of Chem., U.S. Dept. of Agr.; also *Journ. Am. Chem. Soc.*, xxviii., No. 11). In his latest report (*Journ. Am. Chem. Soc.*, 1906), he makes, among others, the following conclusions—"As recommended by the author in the Association of Official Agricultural Chemists, the separation of the proteins of wheat into more than two groups, viz., first, alcohol-soluble, second, alcohol-insoluble, seems unwarranted, both because of the difficulty of making a further quantitative separation, and because of the indefinite value of such separation."

In the light of all data available to the writer, this statement of Chamberlain's seems wholly justified. It is to be hoped, however, that methods may be devised by which an accurate quantitative separation of the wheat proteins may be accomplished.

A large amount of chemical investigation has been conducted during the past ten years with wheat flour, and one of the chief objects in this work has been to determine some relation between the composition of the flour and its strength, i.e., ability to produce a large well piled loaf. An immense number of gliadin determinations have been made in this work, to ascertain if any relation existed between the ratio of gliadin to the total protein, and the strength of the flour. The writer proposes to discuss this matter in detail in a later paper.

The determination of gliadin, or to be scientifically correct, alcohol-soluble protein, in wheat flour, is simple in principle, and duplicate determinations check very closely. It consists, as usually practised, in frequent agitation for several hours of a weighed quantity of flour with a definite volume of dilute alcohol, letting stand over night, and the final determination of nitrogen in an aliquot portion of the filtrate. As has been mentioned, a single operator can get duplicate determinations to check very closely, and like-

wise different operators using exactly the same method will get closely agreeing results. Unfortunately, however, the situation is that different chemists use different methods, and hence their results are in no sense comparable, unless the methods used are accurately described, when the results may be compared provided the methods are essentially the same.

*Bull.* 107, Bureau of Chemistry, U.S. Dept. of Agr., Official and Provisional Methods of Analysis, Association of Official Agricultural Chemists, contains no method for the determination of gliadin or other wheat proteids. Page 59, Sec. VIII., "Methods for the Analysis of Cereal Foods," is blank, except for the heading.

The chief differences in methods used for the determination of alcohol-soluble protein in wheat flour are these:—

1. In the strength of alcohol.
2. In the method of extraction.

What strength alcohol should be used? It is commonly recommended that 70 per cent alcohol be used, but as a rule the reader is left in doubt as to whether 70 per cent alcohol means 70 per cent by weight or 70 per cent by volume. Seventy per cent alcohol by weight has a specific gravity of 0.8729, and is equivalent to 76.91 per cent alcohol by volume. Seventy per cent alcohol by volume has a specific gravity of 0.8898, and is equivalent to 62.45 per cent by weight. There is a difference of 6.91 per cent alcohol by volume, or 7.55 per cent alcohol by weight between alcohol of 70 per cent strength by weight and 70 per cent by volume. Provided 70 per cent alcohol by weight and 70 per cent by volume extracted the same amount of protein from a flour, one might as well be used as the other. In fact, however, there is a considerable difference in the extractive power of these two strengths of alcohol, as will be shown later.

Just why should 70 per cent alcohol (whether by weight or by volume) be used instead of alcohol of some other strength, anywhere from 10 per cent to 95 per cent? Apparently 70 per cent alcohol has been used on the supposition that it would extract a larger quantity of protein than alcohol of any other strength. Osborne makes the following statement ("Proteins of the Wheat Kernel," pub. by Carnegie Inst., 1907, p. 109):—"Exactly what strength of alcohol dissolves the largest proportion of gliadin has never been determined, but the maximum solubility is attained with about 70 per cent of alcohol by volume." Without doubt Osborne considers that alcohol of that strength which will extract the largest amount of protein should be used for the determination of gliadin in wheat flour. In the light of all available data, it seems perfectly logical that alcohol of that strength which will extract the maximum amount of protein should be used for the determination of gliadin in wheat flour.

Some chemists object to using alcohol more dilute than 70 per cent on the ground that the weaker alcohol extracts the larger proportion of non-gliadin protein. This is a weak objection, since it is a rather difficult matter to determine just what strength alcohol will extract the largest amount of true gliadin and the smallest amount of non-gliadin protein. It would certainly seem best to use that strength alcohol which will extract the largest amount of total protein.

A number of investigators have determined the relative amounts of protein extracted from flour by alcohol of different strengths. Shutt (*Bull.* 57, Central Experimental Farm, Ottawa, Can., 1907) determined the amount of protein extracted from flour by alcohol varying in strength from 60 per cent to 75 per cent by weight, with the following results:—

| Strength of alcohol by weight (per cent), | Gliadin (per cent). | Proportion of protein in the form of gliadin. |
|-------------------------------------------|---------------------|-----------------------------------------------|
| 60                                        | 5.36                | 54.0                                          |
| 62.5                                      | 5.30                | 53.4                                          |
| 65.0                                      | 5.24                | 52.9                                          |
| 70                                        | 4.71                | 47.4                                          |
| 75                                        | 3.41                | 34.3                                          |



From this data it will be noted that there is a constant decrease in the amount of protein extracted as the alcohol increases in strength from 60 per cent to 75 per cent by weight. Since 60 per cent alcohol is the lowest strength shown there is no means of knowing just what strength of alcohol would extract the largest proportion of protein.

Sixty-two and five-tenths per cent alcohol by weight corresponds closely with 70 per cent by volume. By looking at the above table it will be noted that 70 per cent alcohol by weight extracts 0.59 per cent less protein than 62.5 per cent by weight, or 70 per cent by volume. The gliadin number with the 70 per cent alcohol by weight is 47.4, while with 70 per cent alcohol by volume it is 53.4. Obviously it makes considerable difference whether alcohol used for the determination is 70 per cent by weight or by volume, or whether alcohol of some different strength is used. Shutt makes special mention of the fact that alcohol used for the determination of gliadin should be prepared with great accuracy, since, as his results show, slight differences in strength of the alcohol materially affect the amount of protein obtained. The above writer uses 70 per cent alcohol by weight for the determinations reported in that bulletin.

Snyder (*Bull.* 105, Bureau of Chem., U.S. Dept. of Agr.) in his report on the separation of vegetable proteins before the Association of Official Chemists, 1906, makes reference to several investigations conducted to determine what strength of alcohol would extract the maximum amount of protein from wheat flour. Teller, of the Arkansas Station, determined the amount of protein extracted from flour by alcohol varying in strength from 40 to 95 per cent, with the following results:—

*Amount of Nitrogen Dissolved by Varying Strengths Alcohol.*

| Alcohol by volume. Per cent. | Alcohol-soluble nitrogen. Per cent. | Alcohol by volume. Per cent. | Alcohol-soluble nitrogen. Per cent. |
|------------------------------|-------------------------------------|------------------------------|-------------------------------------|
| 95                           | 0.21                                | 65                           | 1.30                                |
| 90                           | 0.31                                | 60                           | 1.38                                |
| 85                           | 0.61                                | 55                           | 1.40                                |
| 80                           | 0.89                                | 50                           | 1.40                                |
| 75                           | 1.08                                | 45                           | 1.40                                |
| 70                           | 1.18                                | 40                           | 1.40                                |

It will be noted that the maximum extraction was obtained with 40 to 55 per cent alcohol by volume.

Snyder determined the amount of protein calculated as nitrogen extracted by alcohol, varying in strength from 60 to 70 per cent by weight with the following results:—

*Protein Calculated as Nitrogen Dissolved by 60 to 70 per cent Alcohol.*

| Alcohol (per cent). | Nitrogen (per cent) |
|---------------------|---------------------|
| 60                  | 0.85                |
| 68                  | 0.74                |
| 70                  | 0.70                |
| 72                  | 0.67                |

Shutt also reports results obtained with alcohol varying in strength from 60 to 86.4 per cent by weight, the amount of protein extracted decreasing with the increase in strength of alcohol. The results are as follows:—

*Gliadin Nitrogen Dissolved by Varying Strengths Alcohol.*

| Alcohol. Per cent by weight. | Gliadin nitrogen. Per cent. | Alcohol. Per cent by weight. | Gliadin nitrogen. Per cent. |
|------------------------------|-----------------------------|------------------------------|-----------------------------|
| 60                           | 0.94                        | 75                           | 0.60                        |
| 62.5                         | 0.93                        | 76.8                         | 0.66                        |
| 65                           | 0.92                        | 86.4                         | 0.12                        |
| 70                           | 0.83                        |                              |                             |

On looking over all available data, it appears that Teller is the only one who has determined the solvent

power of alcohol of less strength than 60 per cent by weight. He finds that the protein extracted by alcohol varying in strength from 40 to 55 per cent by volume is practically constant. The other investigators find a gradual decrease in solvent action of alcohol as it increases in strength above 60 per cent. While Teller's work appears conclusive, it was thought worth while to cover the ground even more fully, both as regards strength of alcohol and the method of extraction, in order to obtain the maximum amount of gliadin from flour. The following points were investigated:—

1. Time necessary for maximum extraction.
2. Strength alcohol necessary for maximum extraction.
3. The effect of temperature on the determination of gliadin.

The common method for the determination of gliadin is to extract 2 grms. of flour with 100 cc. neutral alcohol in a glass or rubber stoppered flask for eighteen to twenty-four hours, shake frequently the first three to four hours, then allow to stand over night, filter, and determine nitrogen in an aliquot portion of the filtrate in the usual manner. This method is undoubtedly accurate provided the flask is shaken frequently for some time. The only objection is the time element. In commercial laboratories, where immediate results are wanted, time is an element of considerable importance.

The laboratory of the Minnesota Experiment Station is provided with a soil shaker used for the mechanical analysis of soils. It has compartments for sixteen 8-ounce milk steriliser bottles, has a backward and forward movement, and is run by a  $\frac{1}{4}$  h. p. motor. The following experiment was conducted with macaroni flour to determine the length of time necessary, with constant shaking, to effect a complete extraction of gliadin from flour.

Approximately 5 grms. of flour were weighed into each of five steriliser bottles; 200 cc. neutral 70 per cent alcohol by weight added. Four bottles were placed in the shaker and shaken for periods of thirty, forty-five, sixty, and, ninety minutes respectively. The fifth bottle was shaken by hand at intervals for three hours, and then let stand over two days, making forty-seven hours in all. In the case of samples run in the shaker, filtration was facilitated by running the samples for ten minutes in an electric centrifuge, which gave a clear solution which hardly needed filtering. Nitrogen was determined in filtrate by the modified Kjeldahl method.

*Gliadin Extracted on Shaking for Different Periods.*

| Sample. | Time shaken.                                           | Per cent gliadin N extracted. |
|---------|--------------------------------------------------------|-------------------------------|
| 1.      | 30 mins. . . . .                                       | 0.90                          |
| 2.      | 45 mins. . . . .                                       | 0.95                          |
| 3.      | 60 mins. . . . .                                       | 0.96                          |
| 4.      | 90 mins. . . . .                                       | 1.03                          |
| 5.      | Shook frequently for 3 hours, let stand 44 hours . . . | 0.97                          |

A similar test was run with a sample of soft winter wheat flour, using 70 per cent alcohol by weight, with the following results:—

| Sample. | Time shaken.                                           | Per cent gliadin N extracted. |
|---------|--------------------------------------------------------|-------------------------------|
| 1.      | 60 mins. . . . .                                       | 0.89                          |
| 2.      | 90 mins. . . . .                                       | 0.90                          |
| 3.      | Shook frequently for 3 hours, let stand 15 hours . . . | 0.84                          |

In the first test, shaking for ninety minutes gives slightly higher results than shaking for sixty minutes. Shaking for sixty minutes gives practically identical results with the method (No. 5) where the sample is shaken for three hours, and let stand over night or longer. In test No. 2 practically identical results are obtained where samples are shaken for sixty and ninety minutes respectively. Sample No. 3, using the old method, gives slightly lower results than the first two samples.

These tests show that alcohol-soluble protein can be as completely extracted from flour by shaking the sample vigorously for sixty to ninety minutes in a shaking machine, as when the sample is shaken frequently for two to three hours by hand, and then let stand eighteen hours more or less.

The method now in use in this laboratory for the determination of alcohol-soluble protein in flour is as follows:—Weigh approximately 2 grms. of flour into an 8-ounce milk steriliser bottle, add 100 cc. neutral 50 per cent by weight alcohol; shake in machine for one hour, centrifuge for ten minutes, filter, determine nitrogen in aliquot portion of filtrate by modified Kjeldahl method. Correction is always made for a blank determination run with the alcohol, &c. In using a shaking machine it is, of course, necessary to have the bottles shaken vigorously so that the flour will remain in suspension. The use of the centrifuge makes filtration easy, which would otherwise be rather slow, due to fine flour particles in suspension.

In making up the varying strengths of alcohol reported in this paper, the alcohol table found in Leach was used, and the specific gravity was determined by means of a Sartorius balance. The making up of a definite strength alcohol for the determination of gliadin is definite strength alcohol for the determination of gliadin is a matter of considerable importance. An accurate Westphal or Sartorius balance, or picnometer, should be used, and not a spindle. The temperature at which the reading is taken should, of course, be exactly that for which the alcohol table is intended.

#### *The Effect of Temperature on the Extraction of Gliadin from Flour.*

Opinion differs as to the relative solvent action of cold or boiling alcohol on flour.

Leach ("Food Insp. and Anal.," 1st. Ed., p. 232) gives a method for the determination of gliadin which consists in shaking 1 gm. of flour with 100 cc. 75 per cent hot alcohol, and keeping the mixture at a temperature just below the boiling-point of the alcohol for one hour, shaking frequently. The mixture is then filtered and nitrogen determined in the usual way.

Chamberlain reports results showing that cold alcohol extracts more gliadin from flour than hot alcohol (*Food. Am. Chem. Soc.*, 1906, No. 11).

The following tables show the results of a test conducted in this laboratory to determine the amount of protein extracted by 50 per cent by weight alcohol at different temperatures.

Approximately 2 grms. of flour were weighed into each flask, 100 cc. of cold 50 per cent by weight alcohol added, single tube condensers inserted, and each flask placed in a water-bath at the desired temperature. Samples were shaken frequently during the period of extraction, and were finally allowed to cool before filtering. A baker's patent spring wheat flour was used.

Test No. 1.

| Sample No. | Temperature. | Period of extraction.           | Per cent of gliadin nitrogen. |
|------------|--------------|---------------------------------|-------------------------------|
| 1.         | 35—37° C.    | 4½ hrs., then let stand 14 hrs. | 1.20                          |
| 2.         | 50           | 2½ hrs., then let stand 14 hrs. | 1.19                          |
| 3.         | 60           | 2½ hrs., then let stand 14 hrs. | 1.23                          |
| 4.         | 75           | 2½ hrs., then let stand 14 hrs. | 1.45                          |
| 5.         | 75           | 2½ hrs., then let stand 14 hrs. | 1.58                          |
| 6.         | 25—27        | Shake 1 hr., usual method.      | 1.18                          |

(Test No. 5 made at a different time from Test No. 4).

From this table it appears that there is no increase in the amount of gliadin extracted with rise in temperature, until a temperature just below that at which the alcohol boils is reached. The two samples extracted at 75° C. at different times gave quite different results. Extracting with hot alcohol is more difficult of operation, and does not seem to offer any advantage over extracting in the cold. Unless all extractions are carried on under exactly

the same conditions, extraction with hot alcohol probably will not give as accurate results as our present methods.

#### *Amount of Protein Extracted from Flour with Alcohol of Varying Degree of Strength.*

The following table reports results of tests run to determine the relative solvent action on wheat protein, of alcohol varying in strength from 10 per cent to 75 per cent by weight; and including one extraction with distilled water. The method used for all determinations is the one previously described as being used in this laboratory, all tests being run under exactly the same conditions except as regards strength of alcohol.

#### *Relative Extractive Power of Alcohol of varying Strengths.*

| Alcohol by weight (per cent). | Per cent gliadin nitrogen.   |                     |
|-------------------------------|------------------------------|---------------------|
|                               | Hard spring, baker's patent. | Soft winter patent. |
| Water                         | 0.60                         | 0.51                |
| 10                            | 0.56                         | 0.46                |
| 20                            | 0.57                         | 0.50                |
| 30                            | 0.99                         | 0.78                |
| 35                            | 1.13                         | 0.92                |
| 40                            | 1.16                         | 0.93                |
| 45                            | 1.17                         | 1.02                |
| 50                            | 1.18                         | 1.03                |
| 55                            | 1.13                         | 0.99                |
| 60                            | 1.12                         | 0.96                |
| 65                            | 0.96                         | 0.87                |
| 70                            | 0.90                         | 0.87                |
| 75                            | 0.61                         | 0.54                |

From this table it will be noted that alcohol of 10 to 20 per cent strength extracts less protein than distilled water, and that as alcohol increases in strength from 10 per cent to 50 per cent it extracts more protein. Alcohol varying in strength from 45 per cent to 55 per cent extracts practically the same amount of protein. As the alcohol increases in strength from 55 to 75 per cent its solvent action decreases—the drop being more rapid as the alcohol increases in strength. 75 per cent alcohol extracts about the same amount of protein as distilled water.

The results of this work confirm the work of Teller, who found that alcohol of from 40 per cent to 60 per cent by volume extracted the most protein from wheat flour, and there appears to be no logical reason why alcohol of 70 per cent, whether by weight or volume, should be used for the determination of gliadin, or alcohol-soluble protein in wheat flour. On the other hand, since alcohol of 50 per cent strength by weight extracts as much or more protein than alcohol of any other strength, it would seem perfectly logical that 50 per cent by weight alcohol should be generally used for the determination of alcohol-soluble protein in wheat flour.

As a result of work reported in this paper, the following conclusions seem justified:—

1. For the determination of the alcohol-soluble protein in wheat flour, shaking the sample vigorously and continuously for sixty to ninety minutes in a machine or otherwise, gives equally as high results as when the ordinary method, covering a period of from eighteen to twenty-four hours, is followed.

2. While boiling alcohol extracts slightly more protein than cold alcohol, there does not appear to be any advantage in its use.

3. Alcohol varying in strength from 45 per cent to 55 per cent by weight extracts more protein than alcohol of any other strength, hence it is recommended that 50 per cent by weight alcohol be used for the determination of gliadin in wheat flour, and that the use of 70 per cent alcohol, whether by weight or by volume, be discontinued.—*Journal of Industrial and Engineering Chemistry*, iii., No. 11,



EIGHTH INTERNATIONAL CONGRESS OF  
APPLIED CHEMISTRY,

WASHINGTON AND NEW YORK, SEPTEMBER, 1912.

THE following are the titles of papers to be read before the respective Sections of the Congress:—

SECTION I.—*Analytical Chemistry.*

- James O. Handy, Pittsburgh Testing Laboratory, Pittsburgh, Pa.—Study of the Solubilities of some Metallic Sulphides in Mineral Acids.  
Prof. Victor Lenher, University of Wisconsin, Madison, Wis.—(1) New Colorimetric Method for Titanium. (2) Influence of Lead on the Ferrocyanide Titration of Zinc.  
Prof. Elwood B. Spear, Massachusetts Institute of Technology, Boston, Mass.—Electrolytic Determination of Zinc.  
Frank G. Bryer, New Jersey Zinc Company, Palmerston, Pa.—Modifications in a Rapid Method for Zinc.  
C. T. Bragg, Director of Laboratories, Berry Bros., Ltd., Detroit, Mich.—Delicacy and Accuracy of the Gutzeit Test for Arsenic.  
Prof. S. W. Parr, University of Illinois, Urbana, Ill.—New Bomb Calorimeter, with Special Advantages as to Material of Construction and Method of Operation.  
H. S. Miner, Welsbach Company, Gloucester, N.J.—Determination of Thorium in Rare Earth Minerals.  
Prof. Theodore W. Richards, Harvard University, Cambridge, Mass.—(1) Nephelometry. (2) Control of Temperature in Analytical Operations. (3) Measurement of Temperature in Analytical Operations.  
Hermann C. Lythgoe, State Board of Health, State House, Boston, Mass.—Refractometry.

SECTION IIIc.—*Silicate Industries.*

- Dr. Robert Adan, 33 rue de Flandre, Gant, Belgium.—Propriétés des Ciments Portland Artificielles Belges.  
Ross C. Purdy, Ohio State University, Columbus, Ohio.—Relation between Composition and Structure of Porcelain to Coefficient of Expansion.  
A. S. Cushman, Ph.D., and G. W. Goggeshall, Ph.D., the Institute of Industrial Research, Washington, D.C.—Production of Available Potash from the Natural Silicates.  
Edson S. Bastin, Geologist, U.S. Geological Survey, Idaho Springs, Col.—Natural Silicates in their Relation to Chemical Industry.  
Heinrich Ries, Ph.D., Cornell University, Ithaca, N.Y.—Impurities in High Grade Clays and their Elimination by Washing.  
H. E. Kramm, Cornell University, Ithaca, N.Y.—Effect of Dolomite in Kaolin.  
W. A. Hamor, Research Chemist, Department of Chemistry, the College of the City of New York, New York City.—Development of the Sheet Glass Industry in the United States.  
R. L. Frink, M.E., Expert in Glass and Fuel Economy, Lancaster, Ohio; No. 1031 Columbus Savings and Trust Building, Columbus, Ohio.—Causes of Breakage in Glass Manufacture and Method of Differentiating Chemico-Heterogenic Strains from Cooling Strains (illustrated with lantern slides).  
Samuel R. Scholes, Fellow in Industrial Research, University of Pittsburgh, Research Laboratory, University of Pittsburgh, Pittsburgh, Pa.—Relation between Composition of Glass and its Properties.  
A. V. Bleininger, the University of Illinois, Urbana, Ill.—Effect of Electrolytes upon the Behaviour of Clays.  
Chas. F. Binn, Director, the New York State School of Clay Working and Ceramics, Alfred University, Alfred, N.Y., and C. H. Makeley, the New York

State School of Clay Working and Ceramics, Alfred University, Alfred, N.Y.—Colouring Power of Iron Compounds in Clay Wares.

- Charles F. Binns, Director, the New York State School of Clay Working and Ceramics, Alfred University, N.Y.—Texture and Density of Domestic and Foreign China Clays.  
Allerton S. Cushman, A.M., Ph.D., Director, the Institute of Industrial Research, Washington, D.C.—Notes on a Study of the Temperature Gradients of Setting Portland Cement.  
A. Silverman, Assist. Prof. of Chemistry, University of Pittsburgh, Pittsburgh, Pa.—Criticism of Present Publications on Glass Manufacture, with Specific Illustrations.

SECTION IV.—*Organic Chemistry.*

- Dr. J. Marcusson, Berlin-Lichterfelde W.—Ueber den chemischen Aufbau der hochsiedenden Mineralöle.  
Prof. Dr. Adolf Jolles, Vienna.—Ueber den Zerfall der Kohlehydrate in verdünnter Lösung mit und ohne Anwendung von Oxydantien.  
Dr. Robert Adan, 33 Rue de Flandre, Gand, Belgium.—Composition et analyse des huiles dites "essence" de terebenthine.  
L. H. Friedburg, College of the City of New York.—New Preparation of Nitriles. Some of the Series of Hydrocarbons Represented in Curves.  
W. L. Prager, College of the City of New York.—Esterification of Diaminobenzoic Acid.  
C. Baskerville and W. A. Hamor, College of the City of New York.—Ethers by Catalysis.  
J. H. Ransom and L. D. Hammond, Lafayette, Ind.—Acyl Derivatives of *o*-Amino Thiophenol.  
Dr. Fred Klein, 762 Melrose Ave., Bronx.—Selenium and Tellurium with Special Reference to their Organic Compounds.  
Prof. Dr. M. A. Rosanoff and C. D. Wright, Clark University, Worcester, Mass.—Esterification and Steric Hindrance.  
Prof. Dr. M. A. Rosanoff and R. S. Hart, Clark University, Worcester, Mass.—Formation and Decomposition of Tertiary Amyl Esters.  
Prof. Dr. W. H. Warren and M. R. Grose, Clark University, Worcester, Mass.—Some Derivatives of Fumaric Acid.  
Jerome Alexander, National Gum and Mica Co., 502 W. 45th Street, New York, N.Y.—Rennin Coagulation of Milk from a Colloid Chemical Standpoint.  
Dr. F. D. Dodge, 291, Henry Street, Brooklyn, N.Y.—Oxidation Assay of Essential Oils. New Derivatives of Borneol.

SECTION Vc.—*Fuels and Ashphalt.*

- Dr. Charles Baskerville, College of the City of New York, N.Y.—Oil Shales in America.  
Dr. L. P. Breckenridge, Yale University, New Haven, Conn.—Combustion of Coal in Boiler Furnaces.  
Miss Belle Hill, United States Geological Survey, Washington, D.C.—Natural Gas Industry in the United States.  
Dr. S. P. Sadtler, 39, South Tenth Street, Philadelphia, Pa.—Petroleum Analytical Methods.  
Mr. David White, United States Geological Survey, Washington, D.C.—Resins in Palaeozoic Coals.  
Dr. N. Caro.—By-products of Coke Manufacture.  
Mr. M. R. Campbell, United States Geological Survey, Washington, D.C.—Classification of Coals.  
Mr. Godfrey L. Cabot.—Manufacture and Characteristics of Lamp Black.  
Prof. Charles A. Davis, Bureau of Mines, Washington, D.C.—Peat as Fuel.  
Dr. Metz.—Coal Waste.  
Mr. G. R. Delamater.—Waste of Coal in Bituminous Coal Washings.

- Dr. J. D. W. Frazer and Dr. E. J. Hoffman, Johns Hopkins University, Baltimore, Md.—Soluble Constituents of Bituminous Coal.
- Mr. Frank P. Peterson, Grove City, Pa.—Statistics of Natural Gas Gasoline.
- Dr. O. J. Sieplein, Grove City, Pa.—Analysis of Natural Gas Gasoline.
- Mr. Charles P. Geistle, South Amboy, N.J.—Regulations Affecting Natural Gas Gasoline.
- Mr. Frank P. Peterson, Grove City, Pa.—Uses of Natural Gas Gasoline.
- Mr. Irving C. Allen, Bureau of Mines, Pittsburgh, Pa.—Fuel Oil versus Coals. Diesel Oils. Distillation of Oils. Determination of Sulphur in Fuels. Determination of Water in Fuel Oils.
- Prof. S. W. Parr, University of Illinois, Urbana, Ill.—Meaning of certain Constituents in Coal Ash.
- Dr. H. Wiebe, Physikalisches-Technische Reichsanstalt, at Charlottenburg, Germany.—Ueber die Brauchbarkeitsgrenze des Abel-P.-Apparatus und seine Vergleichung mit dem Pensky Martensschen Flammprüfer.

(To be continued)

## PROCEEDINGS OF SOCIETIES.

## ROYAL SOCIETY.

Ordinary Meeting, March 14th, 1912.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"*New Method of Examining Normal and Diseased Tissues by means of Intra-vitam Staining.*" By Prof. Dr. E. GOLDMANN, University of Freiburg, Baden.

"*Effects of Ultra-violet Rays on the Eye.*" By E. K. MARTIN, M.D.

Three lines of investigation have been taken and carried out, in each case on rabbits:—

1. *Absorption.*—Using an iron arc as the source of light and a quartz spectrograph, the absorption of the media of the eye was found to be as follows:—

Cornea.—All rays of wave-lengths less than 295  $\mu$  are cut off completely.

Lens.—Absorption commences at 400  $\mu$  and is complete beyond 350  $\mu$ .

Vitreous.—Shows a broad absorption band with ill-defined margins extending from 280—250  $\mu$ .

All the media were found to be uniformly permeable to rays between the wave-lengths 660—400  $\mu$ .

2. *Results of Repeated Exposure of Eye to Light containing a High Proportion of Ultra-violet Rays.*—The source of light was a mercury arc enclosed in a quartz tube (Kromayer lamp). A series of animals were exposed at repeated intervals for from three to twelve months. They showed marked inflammatory reaction in the cornea and conjunctiva, and in one case a proliferation of the cells of the anterior lens capsule.

3. *Transmission of Hæmolysins to Aqueous Humour after Exposure of Eye to Short Wave-length Rays.*—The aqueous of animals which have been sensitised to the blood of another species has no power of hæmolyzing red blood corpuscles of that species. After exposure of the eye of such an animal to the quartz mercury-vapour lamp, the aqueous becomes actively hæmolytic and remains so for a period not as yet determined, but in any event longer than the duration of the resulting inflammatory changes.

"*Presence of Radium in some Carcinomatous Tumours.*" By W. S. LAZARUS-BARLOW, M.D., F.R.C.P.

Elsewhere the author published evidence that accelera-

tion of electroscopic leak may be produced by the residue of carcinomatous tissue after its extraction with ether and subsequently with water, or after extraction with acetone. The results were criticised as being small and as possibly explicable by alteration in capacity of the electroscope occasioned by introduction of the substances within it. The subject was therefore re-investigated with an electro-scope of constant capacity in which a fixed wire grating separated the portion containing the gold-leaf from the portion into which the substances were introduced. Twenty-seven samples of primary carcinoma, eight of secondary carcinoma, two sarcomata, and five normal livers and lungs were examined under these conditions, and the original conclusion was confirmed.

Seven of the above specimens were also boiled with HCl and set aside for four weeks in sealed flasks, and at the end of that time were examined in an emanation electro-scope for radium emanation.

The results were as follows:—

| Ref. No.                  | Leak in constant capacity electro-scope<br>N.L.=1. | Divisions per minute due to emanation (emanation electro-scope). |
|---------------------------|----------------------------------------------------|------------------------------------------------------------------|
| Normal liver (437)        | 0.94                                               | —                                                                |
| Primary carcinoma (697 G) | 1.06                                               | 0.004                                                            |
| " (147 C)                 | 1.20                                               | 0.004                                                            |
| " (791)                   | 1.48                                               | 0.068                                                            |
| " (793)                   | 2.24                                               | 1.373                                                            |
| " (697 G)                 | 21.28                                              | 153.5                                                            |
| Secondary carcinoma (440) | 1.29                                               | 0.292                                                            |

Compared with a standard Ra solution these values indicate amounts of radium varying from  $0.188 \times 10^{-8}$  mgrm. to  $2.73 \times 10^{-2}$  per grm. of dried acetone-extracted carcinoma.

The reagents were tested and found radium-free; care was taken to avoid possible contamination with radium, and none of the patients in whose cases radium was found had been treated medically with radium in any way or form.

"*Improved Method for Opsonic Index Estimations Involving the Separation of Red and White Human Blood Corpuscles.*" By CHARLES RUSS, M.B.

"*Electrical Conductivity of Bacteria; and the Rate of Inhibition of Bacteria by Electric Currents.*" By Prof. W. M. THORNTON.

The electrical conductivity of bacteria is measured by observing their orientation when an alternating electric current is passed through a series of saline solutions of graded conductivity containing them. There is no orientation when the conductivity of the liquid is the same as that of the bacteria. The values found range from 35 to 350 ohms per centimetre cube, and depend upon the nature and state of the culture medium. The result of sub-culturing in broth is found to be that the conductivity of the bacteria increases at each step, reaching a steady value at about the fourth sub-culture. Tap water containing *B. coli communis* can be completely sterilised by direct currents in several hours at 0.2 ampère sq. cm. Alternating currents sterilise water nearly if not quite as well as direct currents having the same current-density. In order to obtain well-marked and consistent results, it is necessary to use high current-densities and to have a form of cell with a thin film of liquid which can be readily cooled. Milk is curdled by direct current at the positive pole and thinned at the negative pole. Milk can be sterilised without curdling by passing alternating current, this being largely thermal. The cause of the marked bactericidal action of light is suggested to be syntony between it and the frequency of electronic rotation in the atoms of protoplasm.

"*Clinical Study of Experimental Fever.*" By E. C. HORT, F.R.C.P. Edin., and W. J. PENFOLD, M.B., C.M.

"*Certain Results of Drying Non-sporeing Bacteria in a Charcoal Liquid Air Vacuum.*" By S. G. SHATTOCK and L. S. DUDGEON.



The bacteria used comprised *B. coli*, *B. typhosus*, *Staphylococcus pyogenes aureus*, *B. pyocyaneus*.

Cultures in peptone water were inoculated to slips of glass, and after being allowed to dry in the air were transferred to test-tubes from which the air was exhausted by means of a motor pump, the vacuum being completed by Sir James Dewar's charcoal and liquid air apparatus; the use of mercury was avoided.

The results were compared with those obtained by simple air-drying. The action of light was excluded during the experiments. *B. typhosus* and *B. coli* died both *in vacuo* and in air-dried slips within five days. *S. pyogenes aureus* persists considerably longer under both conditions. The interest centres around *B. pyocyaneus*. Air-dried films did not survive beyond nine days. The slips kept *in vacuo* were alive at seven months. (How much longer this bacterium will live *in vacuo* the authors are testing).

*B. pyocyaneus* was submitted *in vacuo* to the action of heat, and also to the sun's rays (the sealed vacuum tubes being submerged in water). Its resistance to these agencies, in the dried state, *in vacuo*, was not materially, if at all, increased. The bacillus was killed, moreover, by the action of ultra-violet rays on being removed from the vacuum and treated in an atmosphere of nitrogen.

So far as the possibility of interplanetary bacterial life is concerned, it is evident that bacteria in the fully dried state, if free in the interplanetary vacuum, would be killed by the solar light. And as Sir James Dewar's experiments have demonstrated that the ultra-violet rays will kill undried bacteria whilst in the frozen condition at the temperature of liquid air, there is little to support the hypothesis that the living protoplasm on the earth originally immigrated from interplanetary space in a free or uninclosed condition—that free, particulate life has entered the earth's atmosphere, as a result of light propulsion, from extramundane space.

# CHEMICAL SOCIETY.

Ordinary Meeting, March 7th, 1912.

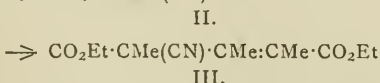
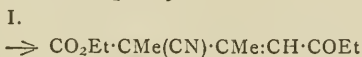
Prof. J. NORMAN COLLIE, Ph.D., F.R.S., Vice-President, in the Chair.

(Concluded from p. 141).

46. "The Chemistry of the Glutaconic Acids." (A Correction). By JOCELYN FIELD THORPE.

In Part I. of this series (*Trans.*, 1911, xcix., 2188) the work previously recorded on the alkylation of esters of the type of ethyl glutaconate was summarised, and it was concluded that under certain conditions the hydrogen atom of the complex X·CH: could be displaced by sodium through the agency of alcoholic sodium ethoxide.

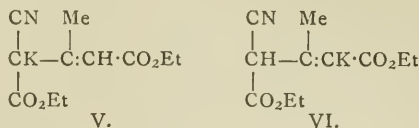
This conclusion was based on the formation of αβγ-trimethylglutaconic acid (IV.) from the ester (III.), which was obtained from the ester (II.) by the action of sodium ethoxide and methyl iodide; the structure of the last named substance being evident owing to its formation from the potassium compound (I.) and methyl iodide:—



IV.

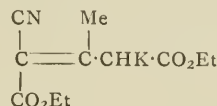
In the original paper (*Trans.*, 1905, lxxxvii., 1674) two possible structures for this potassium compound were considered, namely, V. and VI., and of these Formula V. was regarded as the more probable because of the strongly

negative character of the hydrogen atom displaced. It is, however, evident, in view of the presence of the mobile hydrogen atom which has since been demonstrated, that there is still another possibility, which is represented by Formula VII.:—



V.

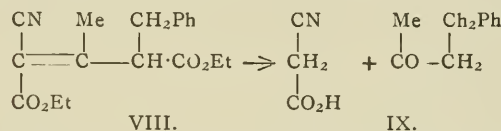
VI.



VII.

In a recent communication (*Trans.*, 1912, ci., 249) it was shown that the esters of substituted glutaconic acids containing the mobile hydrogen atom react with sodium ethoxide, so as to retain this hydrogen, and it is therefore evident that if this statement is true the potassium compound must have the Formula VII., because in order to form a compound of Formula V. the ester would have to part with its mobile hydrogen atom.

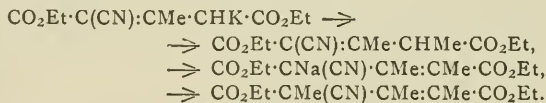
Fortunately, it is a very simple matter to prove that the potassium compound has the structure represented by Formula VII., because, when the metal is displaced by benzyl, an ester (VIII.) is produced, which is hydrolysed with remarkable ease by alkali hydroxide, yielding cyanoacetic acid and benzylacetone (IX.):—



VIII.

IX.

It is proposed to give the full experimental details of this curious reaction in a subsequent communication, but it may be stated here that the benzylated ester (VIII.) exists in two well-defined modifications, one giving a coloration with ferric chloride and dissolving in alkali, the other giving no coloration and being insoluble in alkali. It is the soluble ester only which undergoes disruption in the above manner. There is, then, no reason to assume that the formation of αβγ-trimethylglutaconic acid involves the displacement of the hydrogen atom of the complex X·CH: by sodium, because the course of the reaction can now be represented in the following way:—



That is to say, the introduction of the sodium atom in the second operation, involving as it does the displacement of the mobile hydrogen atom, causes the metal to take up the most negative position in the system (compare *Trans.*, 1912, ci., 249).

The following experimental corrections are therefore necessary:—

*Trans.*, 1905, lxxxvii., 1694, line 21 from top:—The formula of the potassium compound should be  $\text{CO}_2\text{Et} \cdot \text{C}(\text{CN}) \cdot \text{CMe} \cdot \text{CHK} \cdot \text{CO}_2\text{Et}$ .

*Ibid.*, 1695, line 4 from top:—The name of the ester should be ethyl γ-cyano-αβ-dimethylglutaconate, and the formula  $\text{CO}_2\text{Et} \cdot \text{C}(\text{CN}) \cdot \text{CMe} \cdot \text{CHMe} \cdot \text{CO}_2\text{Et}$  or  $\text{CO}_2\text{Et} \cdot \text{C}(\text{CN}) \cdot \text{CMe}(\text{H}) \cdot \text{CMe} \cdot \text{CO}_2\text{Et}$ .

*Ibid.*, 1708, line 18 from top:—The name of the ester should be ethyl γ-cyano-β-methyl-α-ethylglutaconate, and the formula  $\text{CO}_2\text{Et} \cdot \text{C}(\text{CN}) \cdot \text{CMe} \cdot \text{CHEt} \cdot \text{CO}_2\text{Et}$  or  $\text{CO}_2\text{Et} \cdot \text{C}(\text{CN}) \cdot \text{CMe}(\text{H}) \cdot \text{CEt} \cdot \text{CO}_2\text{Et}$ .

47. "The Catalytic Action of Copper at 300° on some Alcohols of the Terpene Group." By GEORGE BALLINGALL NEAVE.

The Sabatier-Senderens test for distinguishing between primary, secondary, and tertiary alcohols (*Bull. Soc. Chim.*, 1905, [3], xxxiii., 263) has been extended to some alcohols of the terpene group. *l*-Borneol was converted into *l*-camphor, fenchyl alcohol into fenchone, and menthol into menthone, all three behaving as secondary alcohols. The following, which are regarded as tertiary alcohols, yielded unsaturated hydrocarbons:—Terpineol and terpin gave dipentene; *isoborneol* gave camphene. *Sobrerol*, which contains both a secondary and a tertiary alcoholic group, was converted into pinol.

48. "Preparation of the Nitrites of the Primary, Secondary, and Tertiary Amines." (Part II.). By PANCHANAN NEOGI.

*Coniinium nitrite* has been isolated, in fairly good yield, from a mixture of the hydrochloride of the base and the alkali nitrites.

49. "Trialkylammonium Nitrites and Nitrites of the Bases of the Pyridine and Quinoline Series." (Part III.). By PANCHANAN NEOGI.

*Coniinium nitrite*, colourless fibrous crystals, sublimes unchanged when heated in a vacuum, and then decomposes with the formation of nitrosoconiine. *Coniine methonitrite* forms a viscous reddish yellow liquid. *Piperidine ethonitrite* crystallises in colourless plates. *Pyridine ethonitrite* is a colourless liquid.

50. "The Glucoside and Oil of *Caesalpinia bonducella*." By KSHITIBHUSHAN BHADURI.

The seeds of *Caesalpinia bonducella* yield an alkaloid, for which the author suggests the name *natin*. The oil has  $D_{20}^{25}$  0.9132, iodine value 96.1, and saponification value 292.8.

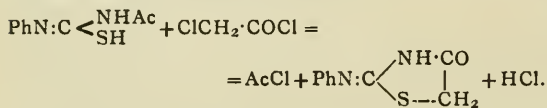
51. "Constituents of *Vernonia anthelmintica*." (Part I.). By KSHITIBHUSHAN BHADURI.

The seeds of *Vernonia anthelmintica* contain a glucoside, to which the name *shomerajin* is assigned. The oil has  $D_{20}^{25}$  0.9731, iodine value 91.7, and saponification value 305.7.

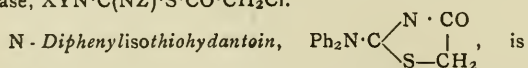
52. "Substituted isoThiohydantoins." By AUGUSTUS EDWARD DIXON and JOHN TAYLOR.

Substituted thioureas (or thiocarbamides), including one or two hydrocarbon radicles, when treated with ethyl chloroacetate, produce the corresponding isothiohydantoins. If, however, the thiourea contains an acyl substituent, interaction does not occur.

On the other hand, chloroacetyl chloride readily attacks thioureas containing an acyl radicle, but not with elimination of two hydrogen atoms; instead, the acyl radicle is expelled (yielding an acid chloride), and the residue, joining with the glycolyl group, forms a non-acylated isothiohydantoin; thus, for example:—



A trisubstituted thiourea, including purely hydrocarbon radicles, X, Y, Z, unites directly with chloroacetyl chloride. In this case, the linking, 'S·CH<sub>2</sub>·CO·', characteristic of the isothiohydantoins, is not produced, but 'S·CO·CH<sub>2</sub>' instead, the resultant compound behaving as the hydrochloride of a base, XYN·C(NZ)·S·CO·CH<sub>2</sub>Cl.



formed when chloroacetyl chloride acts on *n*-benzoyl-*v*-diphenylthiourea, *n*-acetyl-*v*-diphenylthiourea, or *v*-diphenylthiourea; it crystallises from alcohol in brilliant white prisms melting at 198° (corr.).

The phenylisothiohydantoin obtained from *aa*-acetyl-

phenylthiocarbamide and chloroacetyl chloride is the same as that from the *ab*-isomeride; this is attributed to a preliminary transformation of the former variety into the latter during the course of the interaction.

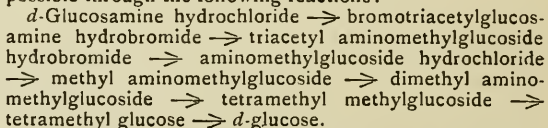
53. "The Conversion of *d*-Glucosamine into *d*-Glucose." (Preliminary Note). By JAMES COLQUHOUN IRVINE and ALEXANDER HYND.

The scheme suggested in a previous paper (*Trans.*, 1911, xcix., 250) for the conversion of *d*-glucosamine into *d*-glucose has now been successfully completed, and, pending publication of the detailed results, the authors consider it advisable to outline the reactions in a preliminary note, in view of the fact that other workers have been engaged on the same subject (*Journ. Am. Chem. Soc.*, 1911, xxxiii., 766).

Glucosamine hydrochloride has been converted, as already described (*loc. cit.*), into methylglucosamine hydrochloride. As this compound is here shown to be definitely related to glucose it may now be termed *aminomethylglucoside hydrochloride*. Like other derivatives of glucosamine, it reacts abnormally with nitrous acid, and although ammonia is evolved when the compound is heated with alkali hydroxides, the reaction seems to be complex, and does not yield methylglucoside. Recourse was therefore had to the silver oxide method of methylation which resulted in the formation of a *methyl aminomethylglucoside* (m. p. 89–90°;  $[\alpha]_D^{20}$  –14.9° in methyl alcohol) as the first definite product. Further methylation gave *dimethyl aminomethylglucoside* as a colourless syrup, from which the substituted amino-group was expelled by heating with barium hydroxide. The product, on exhaustive methylation, was converted into tetramethyl methylglucoside, which was identified by analysis, boiling-point, and specific rotation.

The removal of the methyl-groups was effected in two stages. On hydrolysis with dilute acid, tetramethyl glucose was obtained, and its identity confirmed by analysis, melting-point (85–86°), and by the specific rotation in water ( $[\alpha]_D^{20}$  +82.1°). To complete the series of reactions, the alkylated sugar was reduced to the parent hexose by heating with a 40 per cent solution of hydrogen iodide at 94°. *d*-Glucose, showing the permanent specific rotation  $[\alpha]_D^{20}$  +52.4° was thus obtained in good yield.

The conversion of glucosamine into glucose is thus possible through the following reactions:—



In the course of the work, the salts of aminomethylglucoside were re-examined so as to secure accurate comparison with those described by Fischer (*Ber.*, 1911, xlv., 132). The specific rotations for the hydrochloride and hydrobromide in aqueous solution are now found to be –24.22° and –20.23° respectively, and are thus identical with those found by Fischer. The decomposition points, are, however, 190° and 181°, values which are uniformly 25° lower than those quoted by Fischer. It seems possible that in Fischer's aminomethylglucoside the amino-group is attached to the carbon atom in either the β- or ε-position to the glucosidic group. This assumption would explain the isomerism of the aminomethylglucosides, and is also in agreement with the production from triacetyl bromomethylglucoside of an anhydroglucose capable of forming anhydrophenylglucosazone (Fischer, *Ber.*, 1912, xlv., 456).

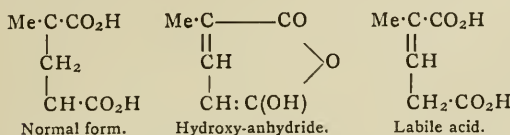
The examination of aminoglucoisides prepared from glucosamine is being continued.

54. "The Chemistry of the Glutaconic Acids. Part IV. The Structure of the Glutaconic Acids." By JOCELYN FIELD THORPE.

The experimental evidence recorded in the previous parts of this series was reviewed, and the conclusion was drawn that the stable forms of the derivatives of glutaconic



acid have a structure similar to that of glutacetic acid itself, in which the tautomeric hydrogen atom is within the three-carbon system and static on the  $\beta$ -carbon atom of this system. The labile acids are those first formed by the hydration of the hydroxyanhydrides, and are in reality the  $\gamma$ -alkyl derivatives of glutacetic acid. The two forms of  $\alpha$ -methylglutacetic acid may therefore be represented in this way:—

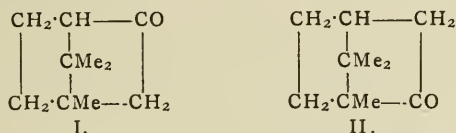


The initial momentum acquired by the hydrogen atom at the moment of its introduction by the hydration of the hydroxyanhydride carries it, if unchecked, into the three-carbon system; if, however, this "spring" is restrained by alkali or casein, the hydrogen is brought to rest within the carbonyl system.

It was also shown that the esters of the glutacetic acids may be of four distinct types, which may be either tautomeric, desmotropic, or structurally different. Examples of all four types have been isolated and identified.

55. "Epicamphor ( $\beta$ -Camphor)." (Preliminary Note). By JULIUS BREDT and WILLIAM HENRY PERKIN, jun.

Epicamphor (I.), the isomeride the ordinary camphor (II.), has been obtained by two processes, namely, (i.) in



small quantities, from camphanecarboxylic acid by bromination, hydrolysis, and subsequent oxidation of the resulting crude hydroxycamphanecarboxylic acid (Lank-shear and Perkin, *Proc.*, 1911, xxvii., 166), and (ii.) from bornylencarboxylic acid by conversion into the azide, and then into aminobornylene, which, on hydrolysis with hydrochloric acid, yields epicamphor in a yield of 80 per cent of that theoretically possible (Bredt and Hilbing, *Chem. Zeit.*, 1911, xxxv., 765). A new and convenient process for the preparation of epicamphor has now been worked out, and is briefly as follows:—

Methyl bornylencarboxylate is converted by the action of hydroxylamine hydrochloride and sodium methoxide into bornylenhydroxamic acid,  $\text{C}_{10}\text{H}_{15}\text{C}(\text{OH})\text{:N}\cdot\text{OH}$ , which melts at  $136^\circ$ , and yields an acetyl derivative melting at  $112^\circ$ . When this hydroxamic acid is heated, it undergoes a remarkable decomposition, yielding epicamphor and ammonia, and the sodium salt of the hydroxamic acid is decomposed by toluene-*p*-sulphonyl chloride with the formation of a syrupy substance, from which epicamphor may be obtained in a yield of 60 per cent of that theoretically possible by treatment with hydrochloric acid and distillation in a current of steam.

Epicamphor melts at  $184$ – $185^\circ$ , and is laevorotatory, having  $[\alpha]_D - 58.24$ ; it yields an oxime (m. p.  $103^\circ$ ) and a semicarbazone (m. p.  $238^\circ$ ).

Bromoepicamphor,  $\text{C}_{10}\text{H}_{15}\text{OBr}$ , obtained by heating epicamphor with bromine in  $100^\circ$ , melts at  $134^\circ$ , and has  $[\alpha]_D - 69.3^\circ$ .

Epiborneol  $\text{C}_{10}\text{H}_{17}\text{OH}$ , is produced when epicamphor is reduced with sodium and alcohol; it melts at  $182$ – $183^\circ$ , and yields a urethane melting at  $82^\circ$ ; it is perhaps a mixture of epiborneol and epizoborneol.

When epicamphor is treated with sodamide and isoamyl nitrite, it is converted into a mixture of two isonitroso-derivatives,  $\text{C}_{10}\text{H}_{14}\text{O:N}\cdot\text{OH}$ , which may be separated by crystallisation from light petroleum. The more sparingly soluble  $\alpha$ -isonitroso-epicamphor melts at  $170^\circ$ , and has

$[\alpha]_D - 201.9^\circ$ ;  $\beta$ -isonitroso-epicamphor melts at  $140^\circ$ , and has  $[\alpha]_D - 184.3^\circ$ , and when it is heated above its melting-point it is converted into the  $\alpha$ -isomeride. Both the  $\alpha$ - and  $\beta$ -isomerides yield camphorquinone on treatment with formaldehyde and hydrochloric acid, and are converted by concentrated sulphuric acid into the imide of camphoric acid (m. p.  $244^\circ$ ).

Aminoepicamphor,  $\text{C}_{10}\text{H}_{15}\text{O:NH}_2$ , is readily obtained when  $\beta$ -isonitrosoepicamphor is reduced in alkaline solution by zinc dust. It separates from light petroleum as a satiny crystalline mass, melts at  $168$ – $170^\circ$ , and has approximately  $[\alpha]_D + 30.15^\circ$ . Experiments on the reduction of  $\alpha$ -isonitrosoepicamphor are in progress.

Epicamphorcarboxylic acid,  $\text{C}_{10}\text{H}_{15}\text{O}\cdot\text{CO}_2\text{H}$ , is produced when sodium or sodamide acts on epicamphor in the presence of carbon dioxide. It melts at  $122^\circ$ , gives a green coloration when ferric chloride is added to its alcoholic solution, and is decomposed, on heating, into epicamphor and carbon dioxide.

Bromoepicamphorcarboxylic acid melts at  $148$ – $150^\circ$ , and is decomposed at this temperature with the formation of the same bromoepicamphor (m. p.  $134^\circ$ ) as is obtained by the direct bromination of epicamphor (see above).

The investigation of epicamphor is being continued in various directions.

## NOTICES OF BOOKS.

*Ship Wiring and Fitting.*\* By T. M. JOHNSON. London: Constable and Co., Ltd. 1911. (1s. net).

This book, which is one of a series of manuals on various types of installations, deals principally with the requirements of ships of the mercantile class; the author has had considerable practical experience in wiring vessels of medium size, and he shows himself to be thoroughly conversant with the subject. He lays special stress on the factors which have to be taken into consideration in work on board ship, such as the atmospheric conditions and the vibration of the ship, and points out the best methods of ensuring the efficiency of the installations. His language is very simple, and his style concise, and the manual contains chapters on wiring for bells, telephones, and electric fans, as well as for lighting.

*The Chemistry of Breadmaking.* By JAMES GRANT, M.Sc.Tech., F.I.C., F.C.S. London: Edward Arnold. 1912. (5s. net).

THE author of this work has found it a difficult task to explain to his readers the facts and principles that they should have learnt in their school days. When the elements of chemistry, physics, and technical mycology are known it is comparatively easy to apply them to the science of bread making, but it is by no means so easy to explain, adequately and yet concisely, for instance, the nature of the organic constituents of cereals to the student who knew nothing whatever of chemistry when he opened the book, or the theory and use of the microscope when the laws of light were quite unfamiliar to him. The earlier parts of the book will in all probability be altogether neglected, or else only very imperfectly understood by the majority of baking students who use the book. On the other hand, those who have had the advantage of learning some science will find that they contain a concise *r  sum  * of the elements of physics and chemistry. The more purely technical chapters are well written, and give a good account of modern practice in bread making, including bakehouse hygiene, and the management of ovens and fuels, while the analysis of cereal foods, malts, flours, sugars, and milk is shortly but clearly treated in the last chapters.

*Denkschrift über die Gründung eines Internationalen Institutes für Chemie.* ("Memoir on the Foundation of an International Institute of Chemistry"). By WILHELM OSTWALD. Leipzig: Akademische Verlagsgesellschaft. 1912.

PROF. OSTWALD writes eloquently in this pamphlet on the benefits which the foundation of an International Chemical Institute would bring to chemists and to the science, and his scheme merits careful attention and consideration. He discusses the need for organising the science, and describes in detail the functions of such an Institute as could fitly be regarded as deserving the epithet "International." He has many practical suggestions to make as to its locality, equipment, and management, and has considered even such details as the subscription for membership and the provision of accommodation for chemists who may want to attend the Institute for purposes of research or for meetings, and although it may be easy to find objections to some of his proposed arrangements there must necessarily be a good deal to criticise in the details of any such scheme, and Prof. Ostwald is doing a valuable work in spreading the knowledge of the growing need for the organisation of the science.

*Mansfield's Oil Gas Apparatus for Laboratories.* List No. 60. Birkenhead. Mansfield and Sons, Ltd.

THIS pamphlet contains an account of the plant necessary for the making of oil gas by Mansfield's apparatus; the working cost is discussed in brief, and some details are given concerning the special appliances used in chemical, physical, and other laboratories. It is claimed that the gas can be made cheaply from any kind of oil, and that it has much greater calorific power than coal-gas, and the opinions of the President and the Professor of Chemistry of the University of Alberta, Canada, where the plant has been installed, are highly satisfactory. The use of the gas would appear to solve the problem of providing means of attaining high temperatures in laboratories which are in comparatively remote spots and cannot be supplied with coal-gas.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Atti della Reale Accademia dei Lincei.*  
Vol. xxi., No. 2, 1912.

**Decomposition of Oximes.**—A. Angeli.—When the oxime of benzophenone is heated to about 180°, nitrogen is evolved. In course of time ammonia is formed, and benzophenone is left. The reaction may be represented by the equations 
$$\begin{array}{c} \text{C}_6\text{H}_5 > \text{C:NOH} = \text{C}_6\text{H}_5 > \text{CO} + \text{NH}_3 \\ \text{C}_6\text{H}_5 \end{array}$$
 
$$3\text{NH} = \text{N}_2 + \text{NH}_3.$$

**Partition of Soda between Boric and Carbonic Acids.**—F. Ageno.—The equation which governs the distribution of caustic soda between boric and carbonic acids is  $\text{H}_2\text{CO}_3 + \text{BO}_2' = \text{HBO}_2 + \text{HCO}_3'$ . The constant  $k = \frac{(\text{HCO}_3')(\text{HBO}_2)}{(\text{BO}_2')(\text{H}_2\text{CO}_3)} = \frac{k_1}{k_2}$  is given by the ratio of the constants of dissociation of the two acids. For carbonic acid at 18°  $k_1 = 3.04 \times 10^{-7}$ , and for boric acid  $k_2 = 1.8 \times 10^{-9}$ . Hence  $k = 178$ . The values found for  $k$  experimentally are very much lower, and decrease as the amount of soda increases. This may be due in the first place to variations in the solubility of the carbonic anhydride, or, secondly, to the increase in the concentration of polyborates as the total concentration of the soda increases.

**Citrophosphate Solutions.**—A. Quartaroli.—The solvent action of ammonium citrate on the phosphates of

the alkaline earths may be explained on the hypothesis of the formation of complex salts, with a corresponding diminution in the alkaline earth cations and the  $\text{PO}_4$  anions. Pratolongo, however, has suggested that a double decomposition occurs. The author has performed a new series of cryoscopic experiments with solutions of ammonium citrate, and has thus obtained results which confirm the hypothesis of the formation of complex salts.

**Anodic Behaviour of Uranium.**—Umberto Sborgi.—The author has studied the electro-chemical behaviour of uranium, using specimens of the metal which were prepared by Moissan's method, and which always contained carbon and nitrogen. The metal is soluble in sulphuric acid and sulphates, in nitric acid and nitrates, in hydrochloric acid and chlorides, in bromides, acetates, and chlorates. In iodides some of the metal dissolves, and some halogen is evolved. The valency of the metal is 4. All experiments in which potential is measured show that uranium—unlike its lower homologues—is not a metal which can assume the passive state.

## MISCELLANEOUS.

**Royal Institution.**—The following are the lecture arrangements at the Royal Institution after Easter:—Dr. Edmund Gosse, two lectures on "Algernon Charles Swinburne—His Early Life and Work"; Mr. F. Balfour Browne, two lectures on "Insect Distribution, with Special Reference to the British Islands"; Prof. W. Bateson, Fullerton Professor of Physiology, R.I., two lectures on "The Study of Genetics"; Prof. W. M. Flinders Petrie, two lectures on "The Formation of the Alphabet"; Prof. A. W. Crossley, two lectures on "Synthetic Ammonia and Nitric Acid from the Atmosphere"; Prof. J. Norman Collie, two lectures on "Recent Explorations in the Canadian Rocky Mountains"; Prof. Howard T. Barnes, two lectures on "The Physical and Economic Aspects of Ice Formation in Canada (the Tyndall Lectures)"; Prof. J. H. Poynting, two lectures on "The Pressure of Waves"; Prof. R. Blomfield, three lectures on "The Architecture of the Renaissance in France, 1494—1661"; Mr. H. Plunket Greene, three lectures on "Interpretation in Song" (with vocal illustrations, accompanist Mr. S. Liddle); Mr. Willis L. Moore, Chief of the United States Weather Bureau, two lectures on "The Development and Utilities of Meteorological Science." The Friday Evening Meetings will be resumed on April 19th, when Mr. Alan A. Campbell-Swinton will deliver a Discourse on "Electricity Supply—Past, Present, and Future." Succeeding Discourses will probably be given by Sir George H. Darwin, Mr. W. C. Dampier Whetham, Prof. W. Stirling, Mr. W. Duddell, Prof. Howard T. Barnes, Sir William MacEwen, and other gentlemen.

## MEETINGS FOR THE WEEK.

MONDAY, April 1st.—Royal Society of Arts, 8. (Cantor Lecture).

"Materials and Methods of Decorative Painting," by Noel Heaton, B.Sc.

Society of Chemical Industry, 8. "Theory of Sulphuric Acid Manufacture," by W. C. Reynolds and W. H. Taylor. "Estimation of Sulphides in Lime Liquors," by J. R. Blockey and P. B. Mehd.

WEDNESDAY, 3rd.—Society of Public Analysts, 8. "Note on the Milk of a Small Herd," by E. Russell. "Separation of Arsenic from Antimony," by S. W. Collins.

"Estimation of Ferric Iron in presence of Organic Matter," by J. T. Hewitt and Gladys R. Mann. "Relation of the Kirschner and Polenske Values in Margarine containing Coconut and Palm Kernel Oils," by E. R. Bolton, H. D. Richmond, and C. Revis. "Convenient Apparatus for obtaining an Average Sample of Gas and for Regulating the Flow of a Gas into an Evacuated Vessel," by F. S. Sinnatt.



# THE CHEMICAL NEWS.

VOL. CV., No. 2732.

## ELECTROLYSIS IN LIQUEFIED SULPHUR DIOXIDE.\*

By L. S. BAGSTER, B.Sc., and B. D. STEELE, D.Sc.

ALTHOUGH considerable attention has been devoted in recent years to the study of the solvent properties of various inorganic and organic chemicals, most of the work that has been carried out has dealt only with the power possessed by various solvents to form conducting solutions and with the relation between this power and certain physical properties of the solvent. Of the large number of investigations of this character, reference may be made to the work of Franklin, Kraus, and others on liquefied ammonia, and especially to those of Walden and his collaborators on a very large number of solvents, both inorganic and organic, and to the investigations of the liquefied halogen hydrides by Steel, McIntosh, and Archibald.

The majority of the above-mentioned investigators have examined the conductivity of solutions in the various solvents, but the behaviour of these solutions during electrolysis has only been examined carefully in the case of solutions in ammonia.

The purpose of the present investigation was to extend our knowledge of some of the lesser-known inorganic solvents, and in particular to determine, if possible, the mechanism of electrolysis in solutions in these solvents. Liquefied sulphur dioxide has been selected as the most convenient solvent to use for two reasons. Firstly, that it is easily obtained in quantity and is liquid at the temperature of boiling ammonia; and secondly, that as a compound containing no hydrogen it should present the greatest possible contrast in its general behaviour to that of water.

The fact that minute traces of moisture profoundly modify the nature of the reaction has interfered with the rapid progress of the investigation, and considerable difficulty has been experienced throughout in carrying out the manipulations on account of the difficulty of excluding moisture.

Ultimately it was found necessary to carry out certain of the experiments *in vacuo* with very carefully dried apparatus and materials.

The electrolysis of the following substances when dissolved in liquefied sulphur dioxide has been investigated—

- Potassium iodide and sodium iodide.
- Trimethylsulphonium iodide.
- Tetramethylammonium iodide.
- Tetramethylammonium sulphate.
- Tetramethylammonium sulphite.
- Hydrogen bromide.
- Mixture of hydrogen bromide and either water or an organic compound.

### POTASSIUM IODIDE AND SODIUM IODIDE.

There appears to be no qualitative difference in the behaviour of these two substances when their solutions are electrolysed. A description of the behaviour of a solution of potassium iodide will therefore be sufficient.

Preliminary experiments were carried out in an apparatus consisting of two glass tubes about 1 cm. in diameter, which were joined together near the bottom by a somewhat narrower tube, the object of the latter being to minimise as far as possible the mixing of the cathode and anode solutions during the experiment.

It was soon found that the resistance of this system was variable and very high when small platinum electrodes were used. When the circuit was first closed, the current, which started at about 200 milliamperes, fell very rapidly to the value of about 1 milliampere. On reversing the current, it rose momentarily to the value of about 40 milliamperes, and again fell very rapidly to about 1 milliampere. On again reversing, the current rose, but never to its original high value. If this process of reversal was repeated a great number of times, it was found that after each reversal the maximum value to which the current rose became less and less, until finally practically no current passed at all at the original potential difference. If the latter was raised considerably, the resistance, which appeared to have been gradually built up, broke down, and the same behaviour could then be repeated at the new voltage. On substituting a fresh pair of platinum-wire electrodes the same behaviour could be repeated, thus indicating that the very high resistance was located at the surface of the electrodes. The cathode at the close of such an experiment was found to be coated with a minutely crystalline dark coloured deposit, which, as the liquefied SO<sub>2</sub> evaporated, became white in colour.

The gradual cutting off of the current is therefore accompanied by the formation of a deposit on the cathode.

At the anode no changes were observed, but the changes which can occur during this experiment are of such a small magnitude, on account of the cutting off of the current, that in all probability iodine, if liberated at the anode, could not be detected.

When an e.m.f. of 40 to 80 volts is applied to the electrodes, it sometimes happens that if the current flowing is large for the first few seconds, gas appears to be evolved at both electrodes, and as long as this happens the current is erratic, but does not fall to the low value which it reaches when no gas is formed.

With larger platinum electrodes of about 1 to 3 cm. area, the changes are very similar, with the difference which might be anticipated, that it takes longer for the current to fall from its initial high to its extremely low value, and that iodine is liberated at the anode and forms there a characteristic red solution in the sulphur dioxide. There is, moreover, little or no evidence of gas evolution.

When mercury electrodes were substituted for platinum, it was found that the general behaviour was the same as before. In this case, however, stirring the liquid electrode caused a rise in value of the current, and at the anode a green compound was formed as a scum on the surface of the mercury. This green substance was probably mercurous iodide.

Experiments with silver and copper cathodes showed that with these the current did not exhibit any of the erratic variations which were found with Pt and Hg cathodes; the silver (or copper) became covered with a dark brown, almost black, deposit, in all probability silver (or copper) sulphide, which, since it is a conducting substance, does not cut off the current. Iodine is liberated both with silver and with copper anodes at the current densities employed.

### Experiments with Anode of other Metals.

*With a Zinc Anode.*—No iodine is liberated except when a high current density is used; with moderate current densities zinc is dissolved and is found afterwards in the solution surrounding the anode.

*With an Anode of Iron Wire.*—The behaviour of the solution appeared to depend on the previous history of the electrode; thus in several experiments it was found that it sometimes happened that iodine was liberated from the anode, whilst at other times, with the same electrode, no iodine would be liberated, but a dark greenish black solution would be formed in the immediate neighbourhood of the anode. This solution could be decolorised by reversing the current, and the presence of iron in the coloured solution was repeatedly demonstrated.

With iron the behaviour is therefore erratic, and suggests

\* A Paper read before the Faraday Society, March 26, 1912.

the ordinary behaviour of iron in aqueous solutions and its passivity of iron.

It is interesting to note that both zinc and iron iodides are only very slightly soluble in liquefied sulphur dioxide, and their solution in the experiments described must be accompanied by the formation of some soluble complex salt with the potassium iodide already in solution.

In the investigation of the electrolysis of potassium iodide in sulphur dioxide two series of quantitative experiments were carried out.

The first had for its object the examination of the properties of the deposit which is formed on the cathode when the solution is electrolysed, and the second the examination of the permanent gas which is liberated at the cathode when current densities of a sufficient magnitude to boil the solution are employed.

#### The Nature of the Solid Deposit.

In these experiments the electrolysis was carried out in an apparatus consisting of a pair of glass tubes of about 2 cm. internal diameter, connected by a narrower tube of about 8 mm. internal diameter. The wider tubes were closed at the top by means of carefully ground glass joints, through which the wires carrying the electrodes were sealed. To one of these ground glass attachments a side tube was sealed containing phosphoric anhydride. Before carrying out an experiment the potassium iodide which was to be dissolved was strongly heated and then placed at the bottom of one of the tubes of the apparatus, the phosphoric anhydride attachment inserted, and the apparatus exhausted. The exhausted apparatus was then heated to 95° C. for about twelve hours. It was then cooled and immersed in a bath of liquefied ammonia and the sulphur dioxide distilled in through a long column of phosphoric anhydride. This general method of procedure was adopted in all the experiments that were carried out, and the effect of dissolved water vapour was in this way eliminated.

The cathode consisted of a piece of platinum foil which could be suspended from the wire which passed through the ground glass stopper, and could be removed and weighed before and after each experiment.

An examination of the cathode after the first experiment showed that the deposit was partially soluble in water, that the solution smelt strongly of sulphur dioxide, and that it contained suspended solid matter which proved to be sulphur, and a series of experiments was therefore carried out in which current was passed through the solution and through a silver voltmeter in series, the object being to determine the relation between the amount of silver deposited in an aqueous solution and the amount of sulphur deposited by the same current in the sulphur dioxide solution.

The results of the experiments are contained in the following table:—

TABLE I.

| No. of experiment. | No. of mgrm. equivalents deposited. |                           |                           | Ratios.                                        |                                                |
|--------------------|-------------------------------------|---------------------------|---------------------------|------------------------------------------------|------------------------------------------------|
|                    | Of Ag in H <sub>2</sub> O solution. | Of K in SO <sub>2</sub> . | Of S in SO <sub>2</sub> . | K in SO <sub>2</sub> . Ag in H <sub>2</sub> O. | S in SO <sub>2</sub> . Ag in H <sub>2</sub> O. |
| 1.                 | 0.58                                | —                         | 0.33                      | —                                              | 0.57                                           |
| 2.                 | 1.06                                | —                         | 0.70                      | —                                              | 0.65                                           |
| 3.                 | 1.15                                | —                         | 0.64                      | —                                              | 0.56                                           |
| 4.                 | Experiment lost.                    |                           |                           |                                                |                                                |
| 5.                 | 0.513                               | 0.483                     | 0.25                      | 0.94                                           | 0.49                                           |
| 6.                 | 0.527                               | 0.495                     | 0.25                      | 0.94                                           | 0.475                                          |

These experiments show conclusively that sulphur is always deposited on the cathode when a solution of potassium iodide is electrolysed, but that it is not possible to obtain quantities corresponding with those indicated by Faraday's law. This is sufficiently accounted for by the known solubility of sulphur in sulphur dioxide.

Qualitative experiments showed that the crystalline deposit on the cathode when dissolved in water and filtered from the separated sulphur, and treated with dilute acids,

yielded sulphur dioxide and a very small quantity of sulphur, and that the solution contained potassium. This indicated that in addition to the sulphur the deposit contained some potassium sulphite and a small quantity of the potassium salt of an acid richer in sulphur, probably potassium thiosulphate. Experiments 5 and 6 of Table I. were therefore carried out to determine the ratio of the equivalent of potassium and silver.

Considering the difficulty of obtaining an adherent deposit on the cathode, these experiments may be taken as indicating the equivalence of the deposit value in the two solutions:—

In several of the experiments that have been described a pair of platinum electrodes was placed in the neighbourhood of the cathode during the experiment, and the conductivity of the solution was measured from time to time during electrolysis. The conductivity fell in every case.

We may summarise the result of this series of experiments as follows:—

1. Sulphur is always deposited at the cathode, but the quantity cannot be accurately determined owing to its solubility in the solvent.

2. A salt deposit consisting largely of potassium sulphite is formed on the cathode in quantities which are equivalent in potassium content to the quantity of silver deposited from an aqueous solution of silver nitrate by the same current.

3. The conductivity of the solution in the immediate neighbourhood of the cathode is lowered during the changes which occur.

The explanation of these facts is immediately forthcoming if we consider them side by side with those which occur at the cathode during the electrolysis of the same salt (potassium iodide) in aqueous solution. This has been done in the following table:—

#### Changes at Cathode during Electrolysis of Potassium Iodide dissolved in—

##### (a) Water.

1. Hydrogen liberated equivalent to Ag in voltmeter.
2. Potassium hydroxide formed equivalent to Ag in voltmeter.
3. Conductivity increased due to increase in salt concentration at cathode from formation of soluble potassium hydroxide.

##### (b) SO<sub>2</sub>.

1. Sulphur liberated.
2. Potassium sulphite (or thiosulphate) formed equivalent to Ag in voltmeter.
3. Conductivity diminished due to decrease in salt concentration at cathode from formation of insoluble potassium sulphite (or thiosulphate).

From this it will be seen that if the liberation of gaseous hydrogen during the electrolysis of aqueous solutions furnishes any evidence for the existence of hydrogen ions in water, the corresponding evidence for the existence of sulphur cations in a solution in liquefied sulphur dioxide is furnished by the liberation of sulphur. Just as in aqueous solution we represent the formation of potassium hydroxide as a combination of the potassium ions which reach the cathode with the hydroxyl ions which have been formed from the water by the discharge of hydrogen ions, so also must we picture the formation of potassium sulphite in sulphur dioxide solutions as a combination of the potassium ions with the minute number of sulphite ions which are formed by the discharge of the sulphur ions.

From these considerations we see that potassium sulphite bears the same formal relation to the solvent sulphur dioxide as potassium hydroxide does to water, but that it is rather to be compared with the insoluble than with the soluble hydroxides, and a closer analogy would be obtained by comparing its formation with that of magnesium hydroxide when a magnesium salt is electrolysed.



*The Nature of the Gas.*

The gas that is evolved in small quantity at the cathode when moist solutions in sulphur dioxide are electrolysed was found to consist of an explosive mixture of hydrogen, oxygen, and nitrogen. When carefully dried materials are used no gas is evolved unless the current density at the cathode is so great that the liquid boils at this point. When this happens a small quantity of gas is evolved, which, after an examination which was prolonged by reason of the difficulty of obtaining and of analysing the small quantities obtained, was proved to consist of a mixture of nitrogen and oxygen considerably richer in nitrogen than ordinary air. It obviously consisted of dissolved air which was boiled out from the solution surrounding the cathode. The hydrogen of the earlier experiments was traced to the presence of traces of water.

ELECTROLYSIS OF TETRAMETHYL IODIDE AND TRIMETHYL-SULPHONIUM IODIDE.

The experiments with these two substances were approached with considerable interest, as it was thought possible that their electrolysis might result in the formation at the cathode of compounds such as ditetramethyl-ammonium and ditrimethylsulphonium. As it was thought that these compounds, even if formed, would probably be unstable at high temperatures, easily decomposed by water, and readily oxidised by atmospheric air, experiments were planned whereby all operations could be carried out at  $-35^{\circ}$  and in a vacuum. As this latter condition involved the continuous pumping away of considerable quantities of  $\text{SO}_2$  a special automatic mercury pump was designed and constructed (Steele, *Phil. Mag.*, June, 1910).

Preliminary experiments showed that in the case of each of these substances there is formed at the cathode a dark blood-red solution, the colour of which is very readily discharged. The conditions necessary for its discharge were first investigated, and it was found that—

- (a) The colour is not discharged by dilution with sulphur dioxide.
- (b) The colour is not discharged by prolonged standing.
- (c) The colour is discharged immediately by the addition of moist liquid sulphur dioxide, and
- (d) Slowly by contact with dry air.
- (e) The colour is discharged and a yellow precipitate formed by mixing together the cathode and anode solutions.

Experiments were therefore planned and the necessary apparatus was designed and constructed to find out, if possible—

- (a) What is the nature of the compound contained in the red solution.
- (b) What is the nature of the yellow precipitate formed on mixing the cathode and anode solutions.

*Investigation of the Nature of the Compound or Compounds contained in the Red Solution.*

Several experiments were carried out, in all of which an apparatus was used which had been specially designed and constructed to admit of the following operations being carried out:—

1. The apparatus and previously heated tetramethyl-ammonium iodide could be exhausted with a phosphorus pentoxide tube attached and left in this condition at  $95^{\circ}$  C. for twenty-four hours to ensure thorough drying of the materials.

2. The solution for electrolysis could be made in the dried apparatus by admitting sulphur dioxide gas through a stopcock and condensing it in the apparatus on to the dried tetramethylammonium iodide. In some of the experiments the sulphur dioxide was previously purified and dried by distilling it from the metal cylinder into a receiver containing phosphorus pentoxide, leaving it in contact with the latter over night, and finally distilling it from this receiver through a long column of phosphorus pentoxide into the electrolysis apparatus.

3. The solution made as described, with complete exclusion of air and moisture, could be electrolysed in an atmosphere of sulphur dioxide at the vapour pressure of the solution, no air being admitted.

4. The red cathode solution, after electrolysis had been carried on for the desired time, could be transferred, without opening the apparatus, into a special receptacle, which could then be sealed off from the main apparatus. The solution in this receptacle then contained the compound or compounds which were to be investigated, and the solution had at no time been subjected to a temperature higher than  $-33^{\circ}$  C. (boiling-point of liquefied ammonia), nor had it been exposed to contact with any substance other than the glass of the containing vessel. It had not passed

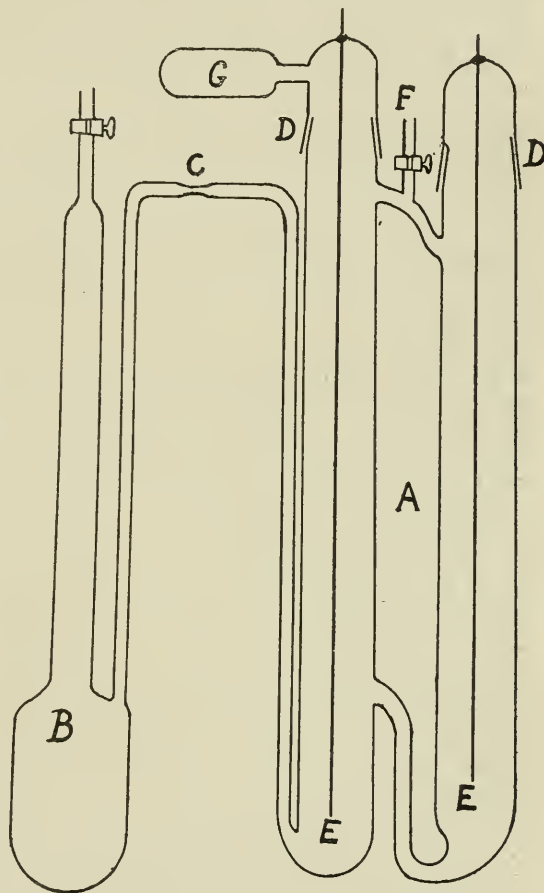


FIG. 1.

through any stopcocks, and therefore could not contain anything but the original salt and the products of its electrolysis.

5. The next stage in the operation was the evaporation of the solution and the examination of the residue. In order to effect the former, the receptacle had been provided with a tube and stopcock. This tube was now attached to the automatic pump, and after the bulb and attachments of the latter had been thoroughly exhausted, the stopcock was opened and the sulphur dioxide removed through the pump, the receiver being kept immersed in a bath of liquefied ammonia.

Fig. 1 represents the type of apparatus used for the electrolysis experiments. The portion B was added when it was desired to separate either anode or cathode solution for examination. The solution could be drawn over from A,

which is the actual electrolysis vessel, into B, by slight variation of the temperature of the two vessels with consequent variation of vapour pressure. B could be sealed off at c by a small blowpipe flame. EE represent the electrodes. DD are ground caps to allow of the insertion of solids and the removal of the electrodes. Sulphur dioxide was distilled in through a tube containing phosphorus pentoxide, sealed to the tap F. G is a phosphoric oxide tube for drying the apparatus.

The possibility that a compound such as  $[N(Me)_4]_2$ , even if formed during electrolysis, might be decomposed during the subsequent evaporation was investigated. Should such a decomposition occur, it is almost certain that the products would include ethane, and accordingly the sulphur dioxide as it was pumped away was tested occasionally to see if any permanent gas could be detected, and in no case was even the smallest trace of such found. It is therefore concluded that no such decomposition occurs.

During the evaporation of the solution the dark red colour is retained until no liquid is left. If the exhaustion is stopped at this stage there remains a solid residue of a very dark brown, almost black substance. At the temperature of the bath the vapour pressure of this substance is about 3.5 mm. of mercury, and on continuing the exhaustion the pressure remains nearly constant at this value, but as the gas is removed from the vessel the colour of the solid substance gradually changes from dark brown to pale yellow. At this stage the gas that was removed was very carefully examined for permanent gases, but none were ever found.

The practical constancy of the sulphur dioxide vapour pressure during exhaustion pointed to the dark brown solid as being simply a compound of the yellow one with sulphur dioxide, and to test this assumption dry sulphur dioxide was admitted to the vessel containing the yellow solid to see if the dark brown substance could be reproduced. It was found that sulphur dioxide was absorbed, but the colour of the compound formed was a pale red. Whether another modification of the original compound or a fresh compound was formed was not determined.

This yellow residue was obtained in about eight experiments, and its properties were examined in various ways. It was found that it never contained more than a trace of iodide, thus showing that separation of the cathode solution had been efficiently carried out. The substance always smelt strongly of sulphur dioxide, was not hygroscopic, and in the case of samples from which the gas had not been continuously pumped away for a prolonged period, it evolved sulphur dioxide on adding to water.

All solutions of the substance were found to leave a residue of sulphur on standing, and some samples rapidly deposited sulphur shortly after solution. The samples which behaved in this manner were found to be very strongly reducing, and gave reactions very similar to those of thiosulphate. The reducing value of the substance was determined by titration with  $N/20$  iodine solution, and the solution after titration was found to be strongly acid. This is the characteristic behaviour of sulphites when titrated with iodine. The amount of sulphite present was determined by combining the results of the iodine and acidity titrations, and the result of the analyses of the different samples is shown in the following summary:—

*Experiment 1.*—Analysis carried out immediately after solution. Iodine reducing value was due to sulphite 87 per cent, and thiosulphate or other reducing agent 13 per cent.

*Experiment 2.*—Analysis made after the solution had stood some time. Reducing action entirely due to sulphite.

*Experiments 3 and 4.*—Analysis made before the deposition of sulphur was complete.

*Experiment 3.*—Reduction due to sulphite 93 per cent. Other substances 7 per cent.

*Experiment 4.*—Reduction due to sulphite 94.5 per cent, and other substances 5.5 per cent.

The substance is obviously composed mainly of tetramethylammonium sulphite, formed at the cathode, together with a small quantity of some extremely easily decomposed and highly reducing substance formed also at the cathode by the interaction of the discharged sulphur. It is probable that the red colour, which is characteristic of this cathode solution and which is so easily destroyed, is a property of this easily decomposed compound.

Similar experiments to those recorded in the foregoing summary were carried out with trimethylsulphonium iodide, and the results, both qualitatively and quantitatively, were the same, namely, a blood-red liquid was formed at the cathode. From this a pale yellow solid was obtained by evaporating off the sulphur dioxide, and this solid, when treated with water, left a residue of sulphur, and the aqueous solution was found to contain sulphite and a very small proportion of a very highly reducing substance which rapidly decomposed with deposition of sulphur.

#### *The Yellow Precipitate formed on Mixing the Cathode and Anode Solutions.*

The anode employed in the foregoing experiments was of zinc, which dissolved during the action, and it was therefore probable that the precipitate was a zinc compound. To test this, a solution of zinc bromide and tetramethylammonium iodide in sulphur dioxide was added to a small quantity of the cathode solution, and an immediate yellow precipitation occurred.

The experiment, in which the compound was prepared, was carried out in an apparatus specially designed and constructed for the purpose of making the solutions by electrolysis, subsequently mixing the cathode and anode solutions and transferring the mixture of solution and suspended precipitate to another specially designed and constructed apparatus in which it could be washed repeatedly with fresh quantities of pure sulphur dioxide, all the operations being conducted in a dry exhausted atmosphere. The precipitate thus prepared was washed seven or eight times, or until the filtrate of sulphur dioxide came through colourless, and it was then dried whilst still in the apparatus, and finally removed for analysis.

The results of the analysis are as follows:—

Sulphur estimated as sulphur dioxide, 19.13 per cent.

Sulphur estimated as sulphate, 20.8 per cent.

Zinc estimated as oxide (two samples), 28.6 and 29.6 per cent.

Theory requires for  $Zn_3(NMe_4)_2(SO_3)_4$  S = 19.3 per cent.  
Zn = 29.5 per cent.

The high result of the sulphur estimation as sulphate might be due to the presence of a small amount of free sulphur in the precipitate, and is in accord with the general experience of the foregoing analyses.

It is interesting to observe the formation of this particular double salt as an insoluble precipitate in liquefied sulphur dioxide, corresponding potassium and ammonium salts having been prepared in aqueous solution and examined by Berglund (*Ber.* 1874, vii., 469).

(To be continued)

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Royal Institution.—A General Monthly Meeting of the Members of the Royal Institution was held on the 1st inst., the Duke of Northumberland, K.G., President, in the chair. Mr. F. C. Tiarks, Mrs. Tiarks, and Mr. A. Wagg were elected members. The chairman reported the decease of Prof. N. Lebedew, of Moscow, an honorary member of the Royal Institution, and a resolution of condolence with the family was passed. The special thanks of the members were returned to Mrs. Ludwig Mond and family for their gift of a bronze medallion of the late Dr. Ludwig Mond, founder of the Davy Faraday Laboratory.



# ON THE ACTION OF THE "LUMINATOR" APPARATUS FOR TREATING HARD-WATER.

By S. SUGDEN.

In this apparatus the hard-water is allowed to flow over a polished aluminium plate, and when used for steam-raising the treated water is found to produce a soft mud instead of the hard scale obtained when untreated water is used. No difference can be detected by analysis between the untreated and treated water, and the aluminium plate does not lose in weight.

It occurred to the author that the "Luminator" treatment might alter the amount of water of crystallisation contained in the calcium sulphate, which is often responsible for the production of hard scales. A piece of polished aluminium foil was placed in a glass jar containing a saturated solution of calcium sulphate, and after an hour the liquid was boiled down to a small bulk. The crystalline residue after air-drying contained much less moisture than the 20.9 per cent required by the formula  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ . The lowest percentage of water obtained was 8.0 per cent. No more water was lost on prolonging the time of exposure to the aluminium.

| Time exposed (hours). | Water (per cent). |
|-----------------------|-------------------|
| $\frac{3}{4}$         | 8.0               |
| 12                    | 8.0               |
| 142                   | 8.0               |

The substance thus obtained crystallised in small needles. On analysis the following figures were obtained:—

|                          | Found<br>(per cent). | Calc. for $3\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$<br>(per cent). |
|--------------------------|----------------------|---------------------------------------------------------------------|
| CaO .. .. .              | 37.6                 | 37.8                                                                |
| SO <sub>3</sub> .. .. .  | 54.0                 | 54.1                                                                |
| H <sub>2</sub> O .. .. . | 8.0                  | 8.1                                                                 |
|                          | 99.6                 | 100.0                                                               |

It thus appears to be a definite hydrate of the formula  $3\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ .

The action of the aluminium is entirely catalytic. After converting between 3 and 4 grms. of calcium sulphate it had lost less than a mgrm. in weight. The author has had no opportunity of analysing the mud from a boiler using "Luminator" treated water, and so cannot be certain that the production of this substance is the cause of the change in the properties of the scale.

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## THE NITRILE OF FUMARIC ACID.

By EDWARD H. KEISER and J. J. KESSLER.

IN 1890 E. H. Keiser (*Am. Chem. Journ.*, xii., 99), starting with solid acetylene diiodide,  $\text{C}_2\text{H}_2\text{I}_2$ , succeeded in making fumaric acid by means of potassium cyanide and caustic potash. Recently E. H. Keiser and L. McMaster (*Am. Chem. Journ.*, xlv., 518; and *CHEMICAL NEWS*, cv., 145) have repeated this synthesis of fumaric acid, and have also made maleic acid synthetically by starting with the liquid acetylene diiodide and treating it with potassium cyanide in alcoholic solution, and then boiling with alkali. In these syntheses the nitriles of the acids must be formed, in the one case the nitrile of fumaric acid and in the other that of maleic acid, and these are subsequently saponified by the alkali. Experiments made to isolate these nitriles were not successful. We have, therefore, attempted to prepare them in another way, namely, by heating fumaramide and ammonium maleate with phosphorus pentoxide. We have succeeded in making the fumaric nitrile, but have not gotten the maleic nitrile. We made the fumaramide in two ways: in the one, we

started with succinic acid and made diethyl monobromsuccinate, and treated this with ammonia, thus obtaining fumaramide, in the other we started with fumaric acid and made the dimethyl ester, which was then converted into the amide by means of ammonia. Both specimens of fumaramide were identical, and when each was heated with phosphorus pentoxide the same sublimate was obtained in each case. This sublimate we find has the composition of fumaric nitrile.

### Fumaramide from Succinic Acid.

Portions of 100 grms. of succinic acid and 25 grms. of red phosphorus were ground together in a mortar until a fine uniform mixture was obtained. This mixture was placed in a dry two-litre flask, provided with a dropping funnel and an exit tube joined to two Woulff bottles containing water to absorb the hydrobromic acid. Bromine was now dropped upon the mixture, the flask being cooled with water, and no attempt was made to hasten the action, which was quite violent at first. For each portion of 100 grms. of succinic acid 454 grms. of bromine were used. The reaction mixture was then allowed to stand twelve hours before distilling off the excess of bromine. This was done by disconnecting one Woulff bottle and attaching a suction pump in its place, and then heating the flask on a water-bath until the excess of bromine and the hydrobromic acid were driven off. This is essentially the method of brominating succinic acid recommended by Volhard (*Liebigs Ann. Chem.*, ccxlii., 144) except that the reaction mixture was allowed to stand longer, and some of the details were modified.

In one case this brominated acid was removed from the flask and weighed. The weight was found to be 300 grms. This included also the metaphosphoric acid which had been formed, and which cannot be separated at this point since it is soluble in the bromsuccinyl dibromide. This bromsuccinyl dibromide fumes strongly in the air, and will, if left in contact with the air, be completely decomposed. When it is allowed to stand in a closed bottle a white layer of succinic anhydride rises to the top, and the heavy oily bromide becomes quite clear, and may be poured off from the anhydride, which forms a crust on top of the oily liquid. The amount of anhydride was not greater than 5 per cent of the total product. In one case more bromine was used, but the increase in the yield of bromsuccinyl bromide was not sufficient to justify this procedure.

Without opening the flask from which the excess of bromine and hydrobromic acid have been distilled 300 grms. of absolute ethyl alcohol are now added drop by drop. The hydrobromic acid given off is absorbed in water in the two Woulff bottles. Care should be taken that the alcohol enters into action as it drops into the flask. If the temperature is low this may not always be the case, and a considerable excess of alcohol will accumulate. If now the flask be shaken a very violent reaction will occur and an enormous amount of hydrobromic acid will be liberated in a short time, thus making the operation a dangerous one. After all the alcohol has been added, which requires several hours, the reaction mixture is again allowed to stand over night, then the excess of alcohol and the hydrobromic acid are removed by distillation on a water-bath, a suction pump being used to diminish the pressure. Water is now added in excess to the diethyl monobromsuccinate. This dissolves the metaphosphoric acid and any excess of alcohol that may remain. After thorough shaking the water solution is poured off by decantation from the ester. This washing is repeated several times, and finally the oily ester is washed with water containing a small amount of bicarbonate of soda to remove the last traces of phosphoric and succinic acids.

To the ester is now added dilute ammonia, made by mixing 450 cc. of water with 50 cc. of concentrated ammonia. The action is allowed to go on for a week, the flask being thoroughly shaken each day. The fumaramide is formed slowly. If the mixture could be continually

shaken it would, no doubt, increase the velocity of the reaction. It is best to wait until the reaction has been entirely completed and no oily ester is left. During the earlier part of the work several separations of the amide were made as it was formed from day to day, but it is difficult to remove the traces of oily ester from it. If the reaction is allowed to proceed to completion the whole may be easily filtered and washed with water, then with alcohol and ether. The amide is not very soluble in alcohol or ether, but it dissolves readily in hot water. It will be observed that until the filtration of the amide all the reactions are carried out in one flask without removing the product that is sought, and it is believed that this procedure helps to increase the yield. From 100 grms. of succinic acid 30–40 grms. of fumaramide are obtained. The theoretical yield is 96.6 grms. This method of preparing the amide cannot be hastened by using more concentrated ammonia or by heating the mixture, as other products are then formed.

#### *Fumaric Nitrile from Fumaramide.*

Five grms. of perfectly dry fumaramide were mixed with 12–15 grms. of phosphorus pentoxide. In order to insure a thorough mixing, the fumaramide was first thoroughly pulverised and the powdered pentoxide added to the fine powder, and the whole thoroughly stirred together. As water is rapidly taken up from the air no time must be lost in placing the mixture in a crystallising dish, covering it with a funnel, and heating the dish on a sand-bath to about 120°. At this temperature the reaction mixture turns black and a miniature snow storm commences in the dish, and the sides of the funnel are quickly covered with a deposit of a fine needle-like sublimate. Care must be taken that the funnel does not become too hot. Cool funnels must be put on from time to time until no more sublimate is obtained. The first funnel contains the nitrile crystals in best condition. The last has a deposit which sticks to the sides of the glass, and which results from the fact that the temperature has risen so high that good crystals are not obtained. The contents of the funnels are removed by tapping them over a sheet of paper, when the crystals fall out. The material that sticks to the sides may be removed by dissolving it in ether and recovered by evaporating the ether.

Fumaric nitrile has a pleasant pungent characteristic nitrile odour. It sublimes very easily. The needle-like crystals are extremely light, and if they are inhaled while floating in the air they prove very irritating to the mucous membranes. If a few of the needles are placed in the bottom of a test-tube and heated they sublime without melting. If, however, a larger amount is used, especially material that has been obtained by the evaporation of the ethereal solution, then the substance melts at 96°. It was thought at one time that two substances were produced in this reaction, one the needle-like crystals, very volatile and subliming without melting, and another substance less volatile and melting at 96°. Further experiments showed that they are identical. The best condition for the formation of the needles is to raise the temperature of the reaction mixture rapidly. With slow heating less is formed. Starting with 5 grms. of fumaramide a yield of 0.15 gm. of fumaric nitrile was obtained.

The analysis gave the following results:—

|           | Calculated for $C_2H_2(CN)_2$ . | Found.    |
|-----------|---------------------------------|-----------|
| C .. .. . | 61.5                            | 61.5      |
| H .. .. . | 2.6                             | 3.1       |
| N .. .. . | 35.9                            | 37.0–35.9 |

The melting-point of the substance prepared from fumaramide and from succinic acid, and also of that prepared directly from fumaric acid as described below, is 96°, and the boiling-point is 186° (760 mm.). It sublimes readily even below 100°, and it is through this property that we have been able to isolate it, as in all cases we have used temperatures lower than the boiling-point.

Fumaric nitrile is easily soluble in water, alcohol, and

ether. When heated with alkalis, ammonia is evolved. The solution of the substance in water gives but a very slight turbidity with silver nitrate. If, however, the solution is heated but a short time with an alkali, and then acidified and silver nitrate added, a copious precipitate of silver cyanide is obtained. The alkali seems to completely decompose the nitrile with the formation of alkali cyanide. Attempts were made to saponify the fumaric nitrile by heating it with dilute sulphuric acid in a sealed tube, and thus to obtain fumaric acid, but they were not successful. The amounts of nitrile used were, however, very small.

#### *Fumaric Nitrile from Fumaric Acid.*

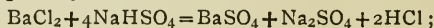
Five grms. of Kahlbaum's fumaric acid was converted into the methyl ester by dissolving the acid in 35 cc. absolute methyl alcohol, conducting a stream of dry hydrochloric acid gas into the solution, and allowing it to stand over night. When the pure crystallised ether was allowed to stand in a 30 per cent solution of ammonia for several days it was transformed into fumaramide.

The pure white fumaramide was filtered, dried, finely pulverised, and mixed intimately with 15 grms. of phosphorus pentoxide. The mixture was quickly put into dry test-tubes, which were then placed into long combustion tubes sealed at one end. The open ends were then sealed and the part containing the test-tubes with the reaction mixture heated in a Carius furnace for forty-eight hours at 130°. Needlelike crystals collected in the cold ends of the tubes. These crystals contained nitrogen, melted at 96°, and had all of the properties of the fumaric nitrile made from succinic acid.—*American Chemical Journal*, xli., No. 5.

### THE PHENOMENON OF OCCLUSION IN PRECIPITATES OF BARIUM SULPHATE, AND ITS RELATION TO THE EXACT DETERMINATION OF SULPHATE.\*

By JOHN JOHNSTON and L. H. ADAMS.

In a previous publication from the Geophysical Laboratory, Carnegie Institution of Washington (E. T. Allen and John Johnston, *Journ. Am. Chem. Soc.*, xxii., 588) it was shown that barium sulphate precipitated from acidified solutions of alkali sulphate and chloride is, in general, contaminated by a number of impurities, the amount of which may be so great as to cause errors in sulphate determinations of 1 per cent or more. Thus, precipitates made from acidified solutions of sodium sulphate and chloride contain, *before ignition*—(a) chloride, almost certainly as barium chloride (see Note); (b) sodium sulphate; (c) sodium hydrogen sulphate; the amounts of these depend upon (1) the composition of the original solution, (2) the method of precipitation, (3) the length of the interval between precipitation and filtration. On igniting the precipitate, the barium chloride reacts with the sodium hydrogen sulphate as follows:—



the hydrochloric acid gas escapes, and along with it is lost some *free sulphuric acid* by decomposition of the sodium hydrogen sulphate, if, as is usually the case, the amount of the latter is more than equivalent to the barium chloride originally present in the precipitate. The precipitates, *after ignition*, therefore contain sodium sulphate (part of which is derived from the sodium hydrogen sulphate), and further may contain in certain cases chloride, most probably as barium chloride. (It is presumed that no barium sulphate was reduced during ignition—a condition easily fulfilled in practice). The presence of chloride in the precipitate tends, of course, to make the analytical results too high; the alkali sulphate, on the other hand, tends to make the results of sulphate determinations too low, since



we are weighing some sodium sulphate, but calculating as if the precipitate were pure barium sulphate. The precipitates from potassium and ammonium salts are entirely similar, except that no ammonium sulphate is found in the ignited precipitate, because it is lost by volatilisation during ignition. The impurities in precipitates made from magnesium salts are similar in character, but smaller in amount.

(NOTE.—It seems to be impossible to determine with certainty whether alkali chloride is present or not; the evidence indicates that, if it is present, the amount must be, in general, relatively small; *cf. loc. cit.*, p. 602, footnote).

It appeared very desirable to extend our knowledge of the nature of such precipitates, first, because of its intrinsic importance, and, second, because of its general interest; for it is highly probable that entirely analogous phenomena are to be met with in the precipitation of many other substances. Consequently the present investigation was undertaken; as a result of which, a fairly complete and satisfactory discussion of the various factors which condition this occlusion is now possible.

We have confined ourselves almost entirely to determinations under standard conditions of the "occlusion," *i.e.*, of the total quantity of sodium sulphate in the ignited precipitate. The "volatility," *i.e.*, the amount of sulphuric acid lost during ignition, which is (with low rates of precipitation at least) a measure of the quantity of sodium hydrogen sulphate present in the unignited precipitate, is, as was shown in the previous paper, affected in the same way as is the "occlusion" by all the conditions, with the exception of the acidity of the original solution. This was to be expected, since we are dealing with the occlusion of sodium sulphate on the one hand, and of sodium hydrogen sulphate on the other; the amount of each depends upon the concentration of undissociated  $\text{Na}_2\text{SO}_4$  and  $\text{NaHSO}_4$  (making the usual assumption that the amount of occlusion is proportional to the concentration of undissociated molecules) (*cf. Richards, Zeit. Anorg. Chem.*, 1900, xxiii., 383); the latter in turn depends upon the concentration of acid in the original solution. Moreover, determinations of "volatility" would have entailed more than double the work.

In order to obtain comparable results on the amount of "occlusion," it is necessary that the work be performed under standard conditions; in the experiments to be described it was our aim to vary only one factor at a time, *e.g.*, the salt content of the original solution was varied, while the acid concentration, the rate of precipitation, and the time of standing before filtration, were kept constant. The procedure followed is identical with that previously described (*cf. Allen and Johnston, loc. cit.*, p. 590; *Journ. Ind. Eng. Chem.*, ii., 198; *Zeit. Anorg. Chem.*, lxi., 108), except that in the case of the heavy metals the amount of metal in the final residue was determined by a suitable method. The results given are in terms of the sulphate of the metal, and represent the amount obtained from one extraction. It is not pretended that the figure after the decimal point is significant; it is given merely as it was actually obtained; some of the figures given represent the mean from duplicate experiments, which did not differ from one another by more than 1 mgm.

In the previous work, it was found that the amount of occlusion is influenced by (A) the concentration of metallic chloride in the original solution; (B) the concentration of hydrochloric acid; (C) the rate of precipitation; and (D) the length of the interval between precipitation and filtration. It may here be said that all the available evidence now indicates that the amount of occlusion is dependent upon (1) the composition of the original solution; (2) the fineness of grain of the precipitate, which in turn is conditioned by the degree of solubility of barium sulphate in the particular medium, the rate of precipitation, and the time and manner of standing between precipitation and filtration. The above factors will now be considered separately.

#### A. Effect of Increasing the Chloride Concentration.

Series of experiments were made as above described, with sodium, lithium, and potassium salts, with the results presented in Table I.

TABLE I.—Experimental Results on the Effect of Added Chloride on the amount of Occlusion of Alkali Sulphate.

|                                                                                                                                          |                              |
|------------------------------------------------------------------------------------------------------------------------------------------|------------------------------|
| Milligrams of alkali sulphate occluded by 2 grms. BaSO <sub>4</sub> .                                                                    |                              |
| Total volume of solution, 350 cc. ; 2 cc. 2 per cent HCl ;<br>time of precipitation, four minutes ; time of standing,<br>eighteen hours. |                              |
| Added chloride (grms.).                                                                                                                  | Occluded sulphate (m.grms.). |
| <i>Sodium.</i>                                                                                                                           |                              |
| 0                                                                                                                                        | 8.2                          |
| 5                                                                                                                                        | 17.4                         |
| 10                                                                                                                                       | 19.0                         |
| 20                                                                                                                                       | 24.4                         |
| 30                                                                                                                                       | 31.4                         |
| 50                                                                                                                                       | 38.4                         |
| 70                                                                                                                                       | 47.6                         |
| 100                                                                                                                                      | 45.8                         |
| <i>Lithium.</i>                                                                                                                          |                              |
| 0                                                                                                                                        | 7.4                          |
| 5                                                                                                                                        | 12.8                         |
| 25                                                                                                                                       | 23.0                         |
| 50                                                                                                                                       | 28.0                         |
| 70                                                                                                                                       | 29.4                         |
| 100                                                                                                                                      | 47.6                         |
| <i>Potassium.</i>                                                                                                                        |                              |
| 0                                                                                                                                        | 11.2                         |
| 5                                                                                                                                        | 13.4                         |
| 10                                                                                                                                       | 16.4                         |
| 40                                                                                                                                       | 25.4                         |
| 80                                                                                                                                       | 35.0                         |

It is evident that an increase in the concentration of chloride in the original solution in each case causes an increase in the amount occluded. With sodium the amount occluded appears to reach a steady value when about 70 grms. of sodium chloride are present; with lithium and potassium, it appears to be still increasing at the greatest concentrations studied.

In view of the similar behaviour of the alkali metals in this respect, and of the fact that these occlusions have no precise or generally applicable physical significance, it seemed sufficient to investigate the occlusion of the other available metals at a few chloride concentrations only. Consequently, the occlusion was determined for each sulphate in solutions (350 cc.) containing initially (a) 0 gm., (b) 5 grms., and (c) 25 grms. of the chloride; the results are given in Table II.

TABLE II.—Experimental Results on the amount of Occlusion of the other Soluble Sulphates.

Milligrams of each sulphate occluded by 2 grms.  $\text{BaSO}_4$ . Conditions as in Table I., except where noted otherwise.

| Metal. | Formula of chloride.                      | Occluded sulphate in precipitates from solutions containing— |                   |                    |
|--------|-------------------------------------------|--------------------------------------------------------------|-------------------|--------------------|
|        |                                           | 0 grms. chloride.                                            | 5 grms. chloride. | 25 grms. chloride. |
|        |                                           | M.grms.                                                      | M.grms.           | M.grms.            |
| Cu ..  | $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ | 13.2                                                         | 17.6              | 21.0               |
| Cd ..  | $\text{CdCl}_2 \cdot 2\text{H}_2\text{O}$ | 32.4                                                         | 41.6              | 63.8               |
| Zn ..  | $\text{ZnCl}_2$                           | 12.8                                                         | 12.2 (a)          | 14.6 (a)           |
| Ni ..  | $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ | 9.6                                                          | 15.4              | 20.6               |
| Mn ..  | $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ | 19.2                                                         | 29.6              | 37.0               |
| Al ..  | $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ | 11.6                                                         | 17.0              | —                  |
| Fe' .. | $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ | 11.4 (b)                                                     | 25.0 (b)          | —                  |
| Mg ..  |                                           | 3.0                                                          | —                 | —                  |

(a) Amount of acid was 5 cc. 20 per cent HCl. With no added chloride and 2 cc. 20 per cent HCl, the occlusion was only 2.6 mgrms.

(b) Amount of acid was 6 cc. 2 per cent HCl.

The figures to which references to footnotes are attached are not strictly comparable with the others; in these cases the addition of a larger quantity of acid was necessary in order to prevent hydrolysis. It proved impossible to make really comparable experiments with solutions containing ferric iron, owing to the hydrolysis of its salts in solutions containing little free acid; there is little doubt, however, that the amount of occlusion of ferric sulphate by precipitates of barium sulphate is of the same order of magnitude as that observed with the other metals. This would cause a greater error in an analysis, however, because the occluded ferric sulphate on heating loses all its sulphur trioxide, and consequently is weighed as oxide; it is better therefore, before precipitating, to reduce the iron to the ferrous state; it is still better to remove the iron entirely, if this course is possible.

In order to facilitate comparison, Table III. was prepared by re-calculation and interpolation of the results contained in Tables I. and II.; the figures given therein represent the number of millimols. of each sulphate (or of each metal) occluded in 1 grm. of a precipitate made from a solution, the equivalent chloride concentration of which was initially (a) 0, (b) 0.1 N, and (c) 0.1 molar.

TABLE III.—Effect of Concentration of the Metallic Chloride on the amount of Occlusion of Metallic Sulphate.

Millimols. of sulphate occluded by 1 grm. BaSO<sub>4</sub> when precipitated from solutions about 0.003 N in HCl, containing the metallic chlorides at the initial concentrations, (a) 0, (b) 0.1 N, (c) 0.1 molar. The final chloride concentration is in each case greater by about 0.025 equivalent normal). Time of precipitation, four minutes; time of standing, eighteen hours.

| Metal.     | Millimols. sulphate occluded by 1 grm. BaSO <sub>4</sub> . |       |       |
|------------|------------------------------------------------------------|-------|-------|
|            | a.                                                         | b.    | c.    |
| Mg .. ..   | 0.024                                                      | —     | —     |
| Li .. ..   | 0.033                                                      | 0.040 | 0.040 |
| Na .. ..   | 0.029                                                      | 0.043 | 0.043 |
| K .. ..    | 0.033                                                      | 0.035 | 0.035 |
| Al .. ..   | 0.017                                                      | 0.02  | 0.03  |
| Fe'' .. .. | 0.037                                                      | 0.06  | 0.09  |
| Ni .. ..   | 0.031                                                      | 0.05  | 0.06  |
| Cu .. ..   | 0.041                                                      | 0.05  | 0.06  |
| Zn .. ..   | 0.040                                                      | 0.05  | 0.06  |
| Mn .. ..   | 0.064                                                      | 0.08  | 0.10  |
| Cd .. ..   | 0.080                                                      | 0.09  | 0.10  |

This table shows that occlusion occurs with all the metals investigated, *i.e.*, with all the common metals, the sulphates of which are soluble in water, that the amount of this occlusion, expressed in mols., is of the same order of magnitude for all the metals, and is nearly identical for similar metals. It is to be noted, however, that the above figures only represent values deduced from a series of experiments in which we attempted to fix all the known variables except the initial chloride concentration, and have no meaning except when the various conditions prescribed are fulfilled. This reservation applies, *mutatis mutandis*, to all the data on occlusion presented in this paper.

In the literature there are a few isolated experiments on the amount of occlusion by barium sulphate precipitated from solutions containing salts; the results, in so far as they are comparable, agree with ours. It has long been known that barium sulphate precipitated from solutions of ferric salts occludes iron in some form (*e.g.*, Jannasch and Richards, *Journ. Prakt. Chem.*, 1889, xxxix., 321). In 1892 this phenomenon was investigated quantitatively by E. A. Schneider (*Zeit. Phys. Chem.*, 1892, x., 425), who obtained results of the same order of magnitude as ours, and found that the percentage amount of iron occluded under given conditions was independent of the total weight of the precipitate; but since his conditions, in so far as they are stated, differ from ours, it is futile to institute quantitative comparison between the results. Others

(Küster and Thiel, *Zeit. Anorg. Chem.*, 1899, xix., 97; xxii., 424; Ostwald, *Zeit. Phys. Chem.*, 1889, xxix., 340; Korte, *Journ. Chem. Soc.*, 1905, lxxxvii., 1503) have since that time repeated and discussed Schneider's data, all of whom doubt his conclusion that this occlusion is a case of solid solution. H. J. M. Creighton (*Zeit. Anorg. Chem.*, 1909, lxiii., 53) investigated the occlusion of aluminium sulphate by barium sulphate, and arrived at results similar to those obtained by Schneider, but again not strictly comparable with ours on account of dissimilarity of the conditions of precipitation. The only other quantitative work known to us along this line is that of Paul Frion (*Journ. Chim. Phys.*, 1909, vii., 101), who studied the occlusion when precipitation was made from solutions containing magnesium nitrate or lanthanum nitrate.

The data presented above suffice to show, we believe, that all of the metals investigated—namely, those with soluble sulphates—are occluded by barium sulphate precipitates; that in each case the amount of this occlusion is of the same magnitude under the same conditions of precipitation, and is similarly affected by similar variation of the conditions.

#### B. Effect of Increasing the Acid Concentration.

The data of the previous paper (*loc. cit.*, Table VI., p. 596), which bear upon this point, have been amplified and extended; the mean results are presented in Table IV., and confirm the conclusion that an increase in the acidity causes a slow decrease in the amount of occlusion. A few isolated experiments bearing on this point made with other metals also confirm this conclusion (see Table II., footnotes).

TABLE IV.—Experimental Results on the Effect of Acid Concentration on the amount of Sodium Sulphate Occluded.

Milligrams. of NaSO<sub>4</sub> occluded by 2 grms. BaSO<sub>4</sub>.

Total volume of solution, 350 cc.; time of precipitation, four minutes; time of standing, eighteen hours; amounts of concentrated HCl and of NaCl as undernoted.

| Solution contains NaCl Grms. | Solution contains 40 per cent HCl in cc. |         |         |         |         |         |
|------------------------------|------------------------------------------|---------|---------|---------|---------|---------|
|                              | 0.1                                      | 0.5     | 2.5     | 5       | 10      | 50      |
| Grms.                        | M.grms.                                  | M.grms. | M.grms. | M.grms. | M.grms. | M.grms. |
| 0                            | 9.0                                      | 8.4     | 7.8     | 4.6     | 3.6     | 2.6     |
| 5                            | 17.4                                     | 13.6    | 11.6    | —       | —       | 3.8     |
| 10                           | 19.0                                     | —       | —       | —       | —       | 4.6     |

#### C. Effect of Rate of Formation of the Precipitate.

It had been observed that the occlusion of sulphate is nearly independent of the rate of addition of the precipitant, or at least of such variations in rate as would occur in analytical practice. (This does not hold for chloride, the amount of which occluded is markedly increased if the whole quantity of the reagent is added quickly, *i.e.*, in a few seconds. This increase is due to the fact that BaSO<sub>4</sub> precipitated quickly is much finer-grained, and consequently absorbs more material). It seemed desirable to test this more thoroughly; accordingly, a series of experiments was performed, in which the two solutions diffused together at such a rate that 2 grms. of barium sulphate were formed in the course of several days.

Various schemes to ensure sufficiently slow diffusion were tried; the method found most satisfactory was to put the requisite amounts of sodium sulphate and of barium chloride into separate small beakers or crucibles; to lower these very carefully—to prevent premature mixing—into a large bulk of solution, contained in a larger beaker, and then to keep this system continuously at 100° by enclosing it in a steam-bath of suitable construction. The solution contained known amounts of hydrochloric acid and sodium chloride; evaporation of solution and condensation of steam were alike prevented by a thin floating layer of paraffin. Under these conditions there formed in the course of some days beautiful transparent



crystals of barium sulphate, many of which were 1 to 2 mm. long. The crystals, after washing until the washings were free from chloride, contained no chloride and less than 0.05 per cent sodium sulphate. This amount does not exceed the probable error in such a determination; consequently, we may conclude that barium sulphate when precipitated *very slowly* at 100° is free from contamination.

A few diffusion experiments were tried at room temperature, which, however, were not so successful. Convection currents set up by temperature fluctuations caused too great a rate of diffusion, and this, combined with the diminished solubility of barium sulphate under these conditions, resulted in the formation of much smaller crystals, which were contaminated to some extent by both chloride and sulphate.

The main purpose in these diffusion experiments was to make large crystals, some physical property of which—as, for instance, the refractive index—might be made to afford information regarding the state in which the impurities are present. This purpose was defeated by the discovery that all of the large crystals of barium sulphate prepared in this way contained no appreciable quantity of impurity.

This observation effectually disposes of the idea that the impurities are present in the form of a solid solution; for, if the concentration of such a solution depends upon the time at all, the variation should be in the direction of an increased concentration, whereas we have found a decrease of concentration with time.

#### D. Effect of Time of Standing.

The data of the preceding paper (*loc. cit.*, p. 596), relating to this point, were confirmed and extended by a series of experiments in some of which much longer intervals elapsed between precipitation and filtration. In another series the precipitate and supernatant liquid were kept at 100° during the whole time.

TABLE V.—Effect of Time of Standing on the amount of Occlusion.

Milligrams. Na<sub>2</sub>SO<sub>4</sub> occluded by 2 grms. BaSO<sub>4</sub>.

Time of standing and temperature during that period as undernoted; other conditions as before.

| Length of interval. | Original solution contained NaCl. |         |         |          |
|---------------------|-----------------------------------|---------|---------|----------|
|                     | 0 gm.                             | 5 grms. | 5 grms. | 10 grms. |
|                     | Temperature about—                |         |         |          |
|                     | 20°                               | 20°     | 100°    | 20°      |
| One-fourth hour ..  | 11.8                              | 22.6    | 22.6    | 27.6     |
| Three hours .. ..   | —                                 | 19.0    | 14.4    | —        |
| Eighteen hours ..   | 9.0                               | 17.4    | 13.4    | 17.8     |
| Two days .. ..      | —                                 | 14.0    | 10.6    | —        |
| Four days .. ..     | —                                 | 12.2    | 10.2    | —        |
| Forty-eight days .. | 8.4                               | 10.4    | —       | —        |
| 150 days .. ..      | —                                 | 8.2     | —       | —        |
| 210 days .. ..      | —                                 | 7.6     | —       | —        |

The mean results, which are presented in Table V., show that the amount of occlusion diminishes notably during the first two days, and progressively, though very slowly, thereafter; that increased temperature causes a greater diminution in occlusion during the first few hours, but is without especial effect thereafter; and that the amount remaining even after long intervals depends on the original amount, and therefore on the composition of the original solution.

The graph obtained by plotting the amounts of occlusion (*m*) against log *t* (*t* being the length of the corresponding interval in days) appears to be a straight line, so that the relation is given by the equation  $m = a + b \log t$ , which is equivalent to the equation  $t = ce^{km}$ . The form of this relation is identical with that of the relations generally used to express diffusion and absorption phenomena. In any case the results of Table V. show conclusively that the amount of occlusion would be entirely negligible if sufficient time were given. This shows again that the figures given by Schneider, and by Creighton, and those contained in the tables of the present paper are not absolute

physical constants (although they are definite enough under definite conditions), and constitute a further proof that we are here dealing with absorption phenomena and not with solid solution, *a fortiori* not with compounds of any description. It is certain that the diminution of the amount occluded could be materially hastened by shaking or stirring; this was not tried, mainly for the reason that such a procedure would generally be impracticable in careful analytical work.

In the previous paper a few experiments on the effect of digesting the precipitates were described, from which it was concluded that the amount of occlusion, at the end of three hours on the steam-bath, is independent of the composition and concentration of the supernatant liquid (*loc. cit.*, p. 597). This conclusion would ordinarily be correct in analytical work where the acid concentration of the solution is not great, but it does not hold if the solution exerts a marked solvent effect upon the precipitate, as *e.g.*, if hydrochloric or nitric acid is present in considerable amount. This is shown by the following experiments.

(To be continued).

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(Concluded from p. 152).

#### SECTION VIa.—Starch, Cellulose, and Paper.

- A. D. Little, 93, Broad Street, Boston, Mass.—Production of Ethyl Alcohol from Cellulose Raw Materials.
- F. P. Dunnington, University of Virginia, Charlottesville, Va.—Grinding of Corn Meal for Bread.
- George L. Bidwell, Bureau of Chemistry, Washington, D.C.—Analytical Methods for the Determination of Starch.
- Dr. Bernhard Herstein, Tariff Board, Treasury Building, Washington, D.C.—Modified Starches, their Properties and Manufacture.
- Prof. Dr. Parrow, Institut für Garungs-gewerbe, Berlin N. 65, See-strasse, Germany.—Dextrines, their Manufacture and Use.
- B. R. Jacobs, Bureau of Chemistry, Washington, D.C. Flour and Bread Making.
- J. Stewart Remington, Aynsme, Grange-over-Sands, Lancashire, England.—Chemical Reactions with Cellulose, and Further Notes in the Theory and Application of Sizing with Rosin Size.

#### SECTION VIIIc.—Bromatology.

- William Frear, Experiment Station, State College, Pa.—Food Standards, their Functions, History, and Forms.
- Charles S. Ash, Chemist and Assistant Superintendent California Wine Association, San Francisco, Cal.—Relation of the Chemist to the Wine Industry.
- Harry Snyder, Chemist Russell-Miller Milling Company, Minneapolis, Min.—Wheat Flour—A Monograph.
- C. F. Langworthy and R. D. Milner.—Respiration Calorimeter as an Aid to the Study of Problems of Vegetable Physiology.
- Paul Rudnick, Armour, and Co., Union Stock Yards, Chicago, Ill.—The Chemist in the Service of the Packing House.
- L. M. Tolman and E. H. Goodnow.—Composition and Manufacture of Cider Vinegar.
- E. M. Chace and A. W. Broomell.—New Methods for the Active Constituents of some of the Essential Oils.
- A. L. Winton, Ph.D., 1605 Heisen Building, Chicago, Ill.—Microscopical Examination of Vegetable Products as an Adjunct to their Chemical Analysis.

- Charles S. Ash, California Wine Association, San Francisco, Cal.—Interpretation of the Results of Wine Analysis.
- H. A. Baker, American Can Company, 447 West Fourteenth Street, New York, N.Y.—Special Adaptation of Iodine Titration Methods for the Estimation of Tin, especially in connection with Determinations of Salts of Tin in Canned Goods. Causes of 'Springers' in Canned Goods.
- Miss M. E. Pennington, Ph.D., Chief of the Food Research Laboratory, 1833 Chestnut Street, Philadelphia, Pa., and Joseph S. Hepburn, A.M.M.S., Assistant Chemist, Food Research Laboratory, 1833 Chestnut Street, Philadelphia, Pa.—Enzymes of the Fat of the Common Fowl.
- W. D. Bigelow and H. E. Patten.—*Rôle of Calcium Sulphate in Phosphate Baking Powders.*
- Estimation of Epinephrine in Suprarenal Glands and in its Solutions Physiologically and by Colour Tests.
- Walter Jones, Ph.D., Johns Hopkins Medical School, Baltimore, Md.—Some New Phases of the Nuclein Fermentation.
- Carl Voegtlin, Ph.D., Johns Hopkins Medical School, Baltimore, Md.—Further Studies in Biologic Oxidations.
- Lyman B. Stookey, Ph.D., University of Southern California, Los Angeles, Cal.—Cambridge Reaction (third paper).
- Charles Baskerville, Ph.D., College of the City of New York, N.Y.—Inhalation Anaesthetics.
- Oswald Schreiner, Ph.D., Bureau of Soils, Department of Agriculture, Washington, D.C.—Physiological *Rôle of Organic Constituents in Plant Metabolism.*

#### SECTION VIII d.—*Physiological Chemistry and Pharmacology.*

- Lafayette B. Mendel, Ph.D., Sheffield Scientific School, New Haven, Conn.—Physiological Behaviour of Lipoid Soluble Dyes.
- Howard S. Reid, Ph.D., Virginia Agricultural Experiment Station, Blacksburg, Va.—Enzyme Activities Involved in certain Plant Diseases.
- Reid Hunt, Ph.D., M.D., Hygienic Laboratory, 25th and E Streets, Washington, D.C.—Physiological Action of some New Compounds of the Choline Type.
- G. A. Menge, Ph.D., Hygienic Laboratory, 25th and E Streets, N.W., Washington, D.C.—Some New Compounds of the Choline Type.
- Atherton Seidell, Ph.D., Hygienic Laboratory, 25th and E Streets, N.W., Washington, D.C.—Comparative Solubility Studies on Thymol and certain other Vermifuges.
- W. H. Schultz, Ph.D., Hygienic Laboratory, 25th and E Streets, N.W., Washington, D.C.—Pharmacological Action of Proteins and some of their Derivatives.
- C. C. Guthrie, M.D., Ph.D., University of Pittsburgh, Pittsburgh, Pa.—A Comparative Study of the Action of Solutions on the Preservation of the Vitality of Tissues.
- Arthur S. Loevenhart, M.D., University of Wisconsin, Madison, Wis.—Further Observations on the Action of Oxidising Substances.
- W. N. Berg, Ph.D., Bureau of Animal Industry, Department of Agriculture, Washington, D.C.—Physicochemical Basis of Muscle Contraction; a Critical Review.
- Jacob Rosenbloom, M.D., Ph.D., 437 W. 59th Street, New York, N.Y.—Chemical and Pharmacological Studies of Human Duodenal Contents.
- George W. Crile, Ph.D., M.D., Medical Department, Western Reserve University, Cleveland, O.—Neurocytological Changes Resulting from the Administration of certain Drugs.
- C. F. Langworthy, Ph.D., Office of Experiment Stations, Department of Agriculture, Washington, D.C.—Study of Problems of Vegetable Physiology by Means of the Respiration Calorimeter; a Progress Report.
- Joseph L. Miller, M.D., Rush Medical College, Chicago, Ill.—Physiological Action of the Various Anatomical Components of the Hypophysis.
- J. A. E. Eyster, M.D., University of Wisconsin, Madison, Wis.—Relation of Calcium to the Inhibitory Mechanism of the Heart.
- W. Worth Hale, M.D., Hygienic Laboratory, 25th and E Streets, N.W., Washington, D.C.
- Atherton Seidel, Ph.D., Hygienic Laboratory, 25th and E Streets, N.W., Washington, D.C.—Comparative
- The Eighth International Congress of Applied Chemistry will be opened by the President of the United States at Washington, D.C., U.S.A., on Wednesday, September 4th, 1912. The other meetings will be held in New York from Friday, September 6th, to September 13th, 1912. There will be many entertainments during the week, and, afterwards, visits will be paid to factories and other places of interest throughout the United States and in parts of Canada.
- As far as possible all papers presented to the Congress will be printed and distributed before the opening session, and must reach Dr. BERNHARD C. HESSE, Secretary, 25, Broad Street, New York City, not later than July 1st next. Rules may be obtained from the Hon. Secretary of the British Organisation Committee as below.
- A preliminary pamphlet (No. 1) was issued in the April 29th number of the *Journal of the Society of Chemical Industry*, 1911. Announcement No. 3, containing general information, programme, details of excursions, and visits to works, with forms of application for membership, may be obtained from CHARLES G. CRESSWELL, Society of Chemical Industry, Palace Chambers, Westminster, S.W.
- Persons contemplating membership in the Congress can obtain membership tickets from the Treasurer of the Congress, WM. J. MATHESON, 182, Front Street, New York City, by forwarding to him an application for membership and the membership fee, which is 5.00 dols.
- Membership tickets can also be obtained from Prof. M. O. FORSTER, Treasurer, British Organising Committee, 84, Cornwall Gardens, London, S.W., who will accept £1 as the equivalent of 5.00 dols.
- Special Steamship Accommodations and Rates.*—Participants in the Congress are urged to reserve their berths for the westward trip at the earliest possible moment, since the steamships are apt to be very crowded at that season of the year. There will be no difficulty in the return voyage. A list of the chief lines sailing from British ports, together with the minimum published rates, can be obtained. Superior accommodation is usually provided at an advance of 20 per cent to 100 per cent on these minimum figures. Second-class rates are not included, although many steamers provide excellent accommodation in this class. For the benefit of members who should not be able to secure accommodation on other steamers, the Executive Committee has purchased a considerable number of berths on the ss. *Cleveland*, sailing from Hamburg on August 22nd, and on the ss. *Philadelphia*, leaving Southampton on August 24th, both expected to arrive in New York several days before the opening of the Congress. Round-trip tickets alone will be sold to members selecting ss. *Cleveland* for westward passage, and the charge will be the lowest possible figure obtainable from the Companies. Participants desiring further information as to the location of the cabins, prices, and other conditions are requested to communicate with the offices of the steamship line selected.



# PROCEEDINGS OF SOCIETIES.

## ROYAL SOCIETY.

Ordinary Meeting, March 21st, 1912.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"Self-Induction of Electric Currents in a Thin Anchoring." By Lord RAYLEIGH, O.M., F.R.S.

"After-Luminosity of Electric Discharge in Hydrogen observed by Hertz." By Hon. R. J. STRUTT, F.R.S.

Hertz observed that if Leyden jar discharges were passed through hydrogen at a pressure of say 100 mm., the gas remains luminous for a small fraction of a second afterwards. His method of experimenting was to allow the gas from the discharge tube to be projected into another vessel by the explosive action of the discharge. The after-luminosity was in this way isolated from the discharge and observed in the auxiliary vessel.

Hertz did not succeed in determining the exact conditions for obtaining this effect with certainty. It is shown in the present communication that the afterglow shows a sulphur spectrum—that developed in the flame of burning carbon disulphide, or, better, by sulphur vapour in a stream of active nitrogen.

By cooling an annexe to the apparatus in liquid air the blue glow disappears, and is restored on heating up. The constituent responsible for it has been frozen out in this treatment, and the pure hydrogen remaining gives no afterglow whatever.

It is concluded therefore that Hertz's effect is due to the presence of sulphuretted hydrogen in the hydrogen employed. It appears to be an exceedingly sensitive test for the presence of this gas. If a bubble of sulphuretted hydrogen is admitted the apparatus gets grossly contaminated, and sulphur gets deposited on the glass walls. After this it is impossible to get rid of the glow by freezing.

Greenish-blue coloured glows kindred to the above are obtained if selenium or tellurium are introduced.

It is conjectured that sulphuretted hydrogen is decomposed by the discharge, that sulphur vapour emerges in a specially active state, and that it then unites with hydrogen, the blue glow accompanying this process.

"Changes in the Dimensions of a Steel Wire when Twisted, and on the Pressure of Distortional Waves in Steel." By J. H. POYNTING, F.R.S.

In a former paper (*Proc. R. S., A*, 1909, vol. lxxxii.) the author described experiments showing that when a loaded wire is twisted it lengthens by an amount proportional to the square of the angle of twist. In this paper it is shown that if the wire is previously straightened by heating it under tension, the lengthening is, within errors of measurement, the same for all loads which could be applied, so that, as was supposed, the only function of the load in the earlier experiments is to straighten the wire. In all wires examined so far the lowering is symmetrical about a point a fraction of a turn always in the counter-clockwise direction from the condition of no twist.

The wire was enclosed in a narrow tube filled with water. It was fixed to the bottom of the tube and passed out from the top through a leather washer. The water rose in a side capillary tube connected to the tube containing the wire, and the changes in level of the water in the capillary tube showed the changes in volume of the wire when twisted. It was found that the contraction of the radius on twisting was also proportional to the square of the angle of twist dating from a point on the counter-clockwise side of no twist, but not the same point as that of symmetry for the lengthening.

The apparatus allowed Poisson's Ratio to be measured. A theory of the changes in dimensions on twisting is given

which appears to account for the experimental results when a single wire is dealt with. In this theory an analysis of the stresses in a finite pure shear strain is given, more complete than that in the former papers; also an analysis of the strains in a finite pure shear stress by equal and opposite torques. Two secondary elastic coefficients are introduced which appear necessary when we take account of the square of the shear, and the experiments give the value of these.

It is shown that if the theory is correct, the pressure in the direction of propagation of distortional waves in steel of the same quality as that of one wire used is 2.5 times the energy per unit volume in the distortional waves, and that the distortional waves must be accompanied by longitudinal waves.

"Orthobaric Densities and Critical Constants of Xenon." By H. S. PATTERSON, R. S. CRIPPS, and R. WHYTILAW-GRAY.

Using a carefully purified sample of xenon prepared from 150 cc. of the gas lent by Sir William Ramsay, measurements were made of the orthobaric densities between the temperature limits of 16 and  $-66.8^{\circ}$  C. The variation of the mean density of liquid and saturated vapour with temperature was found to follow closely Cailletet and Mathias' law, and the results are expressed by the equation,  $D_t = 1.205 - 0.003055t$ ; where  $D_t$  = mean density at  $t^{\circ}$  C.

The slope of the diameter is abnormally large, and is practically identical with the value for the argon diameter recently found by Onnes. The constants  $T_c = 16.6^{\circ}$  C. and  $P_c = 58.2$  atms. were found, and the following were calculated from the results:—

Critical density 1.115 grms. per cc.

Density of liquid close to boiling-point  $3.063$  grms. per cc.

Atomic volume close to boiling-point  $42.7$  grms. per cc.

During purification it was noticed that a mixture of oxygen and xenon, when submitted to the action of the electric discharge, behaved differently to the unsparked mixture of the two gases. Before sparking pure xenon could be separated from such a mixture by condensation and removal of the oxygen by pumping. After sparking the xenon was found to retain a small quantity of oxygen which could only be removed by chemical methods. This association of the two gases is regarded as essentially physical rather than chemical.

"Experimental Work on a New Standard of Light." By W. A. HARWOOD, M.Sc., and J. E. PETAVEL, D.Sc., F.R.S.

The source of light consists of a strip of platinum heated by an electric current. The thermopiles measure the radiation passing through (a) a plate of black flourspar, (b) a water-trough. The thermopiles are connected in opposition. As the current through the strip is increased, the intensity of the luminous radiation increases more rapidly than the intensity of the radiation of longer wave-length. Therefore, for a given thickness of the absorbing media and distance of the thermopiles, there will be one definite temperature at which the reading of a galvanometer in the thermopile circuit will be zero. A long series of experiments showed that the light could be kept constant within  $\pm 0.5$  per cent when a constant temperature was maintained by the above criterion. It was intended to use the method to establish a secondary standard of light which would not be subject to the periodic fluctuations of flame standards or the gradual decay on incandescent standards. The investigation showed, however, that exceptional care and manipulative skill were required to maintain the apparatus in good working order, and from a practical point of view this defect probably outweighs the advantages gained.

"Distribution of the Scattered Röntgen Radiation." By J. A. CROWTHER.

Experiments have been made to determine accurately the distribution of the scattered Röntgen radiation round a radiator. It has been found that the radiation can be

divided into two parts—a true scattered radiation, distributed in accordance with the usually accepted theory of the scattering, and an additional or excess radiation. The curves representing the distribution of the latter have been found to resemble those previously obtained for a parallel pencil of  $\beta$ -rays after passing through thin sheets of matter. The constants of the curves have been determined for primary rays of different qualities and for radiators of different materials. As the primary rays become harder the whole intensity of the excess radiation for a given radiator becomes less, and the angle with the primary beam, at which its intensity reaches a maximum value, becomes smaller. The intensity of the excess radiation becomes greater as the atomic weight of the radiator is increased. Within the limits of the experimental error the quality of the radiation is the same as that of the primary beam producing it.

"Passage of Homogeneous Röntgen Rays through Gases." By E. A. OWEN.

1. The absorption coefficient of the different homogeneous radiation in a light gas, such as  $\text{CO}_2$  or  $\text{SO}_2$ , is proportional to the absorption of radiations in air.

2. The absorption of homogeneous radiation in a gas is proportional to the pressure of that gas.

3. For the homogeneous rays emitted by metals of atomic weight ranging from that of iron to that of molybdenum, the coefficient of absorption in the gases investigated is approximately inversely proportional to the fifth power of the atomic weight of the radiator which emits that characteristic radiation, i.e.,  $\lambda \propto \omega^{-5}$ .

4. The amount of ionisation produced in a thin layer of a gas is directly proportional to the pressure of the gas.

5. The ionisation relative to air is approximately constant in the same gas for the different homogeneous rays.

6. The total number of ions produced by homogeneous beams of equal intensity is approximately the same in each gas for any particular type of rays.

"Fluorescent Röntgen Radiation from Elements of High Atomic Weight." By J. C. CHAPMAN.

"Nature of  $\gamma$ -Rays excited by  $\beta$ -Rays." By J. A. GRAY.

A determination has been made of the relative amount of emergent and incident  $\gamma$ -radiation excited in "radiators" of different thicknesses and different materials. Results of the experiments are:—

1. The emergent  $\gamma$ -radiation is generally greater in amount than the incident radiation, and is more penetrating.

2. The ratio of emergent to incident  $\gamma$ -radiation is greater, for radiators of the same material, the thinner the radiator; for radiators of different materials thick enough to stop the  $\beta$ -rays the lower the atomic weight of the radiator.

3. The results obtained point to the conclusion that the excited  $\gamma$ -ray is an entity, the direction of which is nearly that of the  $\beta$ -ray exciting it.

4. The chance of a  $\beta$ -ray making a  $\gamma$ -ray is roughly proportional to the atomic weight of the radiator, provided the  $\beta$ -ray spends its range in the radiator.

Action of Potash on Tetrolic Acetal.—P. L. Viguier.—Dry potash gives with tetrolic acetal at  $150-200^\circ$  a substance of formula  $\text{C}_6\text{H}_8\text{O}$ . It yields with ammoniacal silver nitrate a white precipitate,  $\text{C}_6\text{H}_7\text{OAg}$ , which is explosive. It is rapidly hydrolysed by dilute acids in the cold. The solution obtained has a very penetrating odour, and reduces silver nitrate and Fehling's solution. When the solution is allowed to stand it gradually loses its odour, and crystals of triacetylbenzene are deposited. Apparently the original substance has the constitution  $\text{CH}\equiv\text{C}-\text{CH}(\text{OC}_2\text{H}_5)_2$ , and gives on hydrolysis the aldehyde,  $\text{CH}\equiv\text{C}-\text{CH}_2-\text{CHO}$ . This then fixes water, giving acetyl acetic aldehyde,  $\text{CH}_3-\text{CO}-\text{CH}_2-\text{CHO}$ , which spontaneously polymerises to triacetylbenzene.—*Comptes Rendus*, cliv., No. 4.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. cliv., No. 4, January 22, 1912.

Degradation of Spartein. Formation of Hydrocarbon Sparteilene.—Charles Mourcu and Amand Valeur.—When methylhemisparteilene,  $\text{C}_{15}\text{H}_{22}\text{N}-\text{CH}_3$ , is subjected to the action of methyl iodide, a mixture of at least two isomeric substances is formed. This mixture is transformed by silver oxide into quaternary ammonium hydrate which yields dimethylhemisparteilene,  $\text{C}_{15}\text{H}_{21}\text{N}(\text{CH}_3)_2$ , *in vacuo* at  $70^\circ$ . An inactive iodomethylate is obtained by the action of methyl iodide on this substance, and the corresponding ammonium hydrate decomposes *in vacuo* at  $75^\circ$  giving sparteilene,  $\text{C}_{15}\text{H}_{20}$ . The degradation of sparteine is thus effected by five successive iodomethylations, or rather by six, since one of them is double. The following intermediate products are formed:—Methylsparteine,  $\text{C}_{15}\text{H}_{25}\text{N}_2(\text{CH}_3)$ ; dimethylsparteine,  $\text{C}_{15}\text{H}_{24}\text{N}_2(\text{CH}_3)_2$ ; methylhemisparteilene,  $\text{C}_{15}\text{H}_{22}\text{N}(\text{CH}_3)$ , and trimethylamine; dimethylhemisparteilene,  $\text{C}_{15}\text{H}_{21}\text{N}(\text{CH}_3)_2$ ; sparteilene,  $\text{C}_{15}\text{H}_{20}$ , and trimethylamine.

Catalytic Formation of Ether Salts of Acids from Formic Ethers.—Paul Sabatier and A. Mailhe.—In presence of titanic oxide formic ethers are decomposed into alcohol and carbon monoxide, and if another acid of the formic acid series is present the corresponding ether salt is formed. Thus from isobutyric acid and methyl formate methyl isobutyrate is obtained. Thorium oxide can also be used as a catalyser, but higher temperatures have to be employed.

Synthetic Formation of Nitrogen Monoxide.—Camille Matignon.—When the heat of reaction and some physical constants of the gases involved are known, the equilibrium of the system  $2\text{N}_2\text{O} = 2\text{N}_2 + \text{O}_2$  can be determined. Thus it is found that if it were possible to attain a temperature of  $3000^\circ$  and a pressure of 3000 atmospheres, and if, moreover, the cooling of the heated gases could be effected quickly enough, it would be possible to obtain nitrogen monoxide synthetically.

Heat of Formation of Silicates.—D. Tschernobaeff and L. Wologdine.—The authors have studied the heat of formation of various silicates and aluminosilicates, by burning mixtures of the substance under investigation and wood charcoal in a Mahler's calorimetric bomb, and finding the difference between the quantity of heat disengaged by burning the carbon and the observed quantity. The results were as follows:—

|                                                           |         |           |
|-----------------------------------------------------------|---------|-----------|
| $\text{SiO}_2 + \text{CaO}$                               | .. .. . | $= +17.4$ |
| $\text{SiO}_2 + 2\text{CaO}$                              | .. .. . | $= +28.7$ |
| $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 + 3\text{CaO}$ | .. .. . | $= +50.2$ |
| $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 + 3\text{CaO}$ | .. .. . | $= +38.2$ |
| $\text{SiO}_2 + \text{Al}_2\text{O}_3$                    | .. .. . | $= -12.0$ |

Thus the heat of formation of anhydrous kaolin,  $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3$ , is negative.

New Alkaline Phosphides.—Louis Hackspill and Robert Bossuet.—When a mixture of an excess of alkali metal and phosphorus is heated *in vacuo* to  $400^\circ$  a black substance is obtained. It slowly decomposes, losing metal, and finally gives a phosphide of formula  $\text{P}_3\text{M}_2$ . The composition of the phosphides of caesium, rubidium, potassium, and sodium is the same, and all of the compounds are yellow powders which are very readily decomposed in the air.

Constitution of Glycerophosphoric Acid.—P. Carré.—The etherification of glycerin with phosphoric acid or monosodium phosphate gives chiefly  $\alpha$ -glycerophosphoric acid,  $\text{PO}(\text{OH})_2(\text{O} \cdot \text{CH}_2 \cdot \text{CHOH} \cdot \text{CH}_2 \cdot \text{OH})$ . Hanriot has already observed that the etherification of glycerin by an equimolecular quantity of hydrochloric acid gives chiefly the  $\alpha$ -monochlorhydrine, with only a very small quantity of  $\beta$ -monochlorhydrine.



# THE CHEMICAL NEWS.

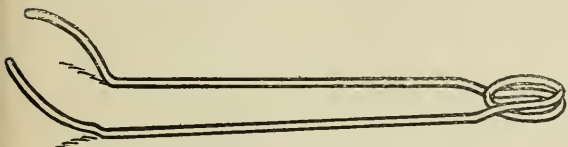
VOL. CV., No. 2733.

## A SIMPLE FORM OF CRUCIBLE-TONGS.

By H. L. BOWMAN, D.Sc.

THE accompanying figure shows a form of crucible-tongs which has been used by the writer for some years for handling crucibles, &c., in analytical work, and has proved so convenient that it appears worth while to publish a description of it.

The tongs are made of a piece of stout wire, coiled into a spring at the middle and bent up at the ends to form two semicircular jaws, which lie in a plane at  $45^\circ$  to the plane of the legs. They are about  $6\frac{1}{2}$  ins. long, and may be



made of bright iron wire of about 0.09 in. thickness, or of the bronzed wire used for sofa-springs. If desired, nickel wire may be used; but in this case the thickness should be somewhat greater, to give sufficient stiffness.

The springiness of the legs enables a platinum or porcelain crucible (with its lid on) to be grasped firmly without fear of damage, while the oblique position of the jaws permits it to be readily lowered into a desiccator or inserted through the door of the balance-case. The tongs are also convenient for lifting watch-glasses or small basins, which rest securely on the ring formed by the partly closed jaws.

University Museum, Oxford.

## ELECTROLYSIS IN LIQUEFIED SULPHUR DIOXIDE.\*

By L. S. BAGSTER, B.Sc., and B. D. STEELE, D.Sc.

(Concluded from p. 160).

### ELECTROLYSIS OF TETRAMETHYLAMMONIUM SULPHITE.

FOR these experiments a sample of tetramethylammonium sulphite was prepared from the iodide by first precipitating the latter with moist silver hydroxide, filtering off the silver iodide, and evaporating the bulk of the water from the filtrate.

The very concentrated solution of tetramethylammonium hydroxide was then placed in the apparatus in which the electrolysis was to be carried out, and sulphur dioxide passed in in sufficient quantities to combine with all the tetramethylammonium hydroxide and to displace all the air. The apparatus was then exhausted, after being connected to a tube charged with phosphoric anhydride. When all the water had been removed sulphur dioxide was distilled into the apparatus so as to make with the dry sulphite a water-free solution for electrolysis.

The sulphite is freely soluble in sulphur dioxide, forming a deep yellowish red solution. On electrolysis, the characteristic blood-red solution containing sulphur is formed at the cathode.

Tetramethylammonium sulphate is also soluble in sulphur dioxide, forming a good conducting solution, which on electrolysis yields the same characteristic red cathode solution as is produced by the iodide and sulphite.

### ELECTROLYSIS OF HYDROGEN BROMIDE.

Hydrogen bromide appears to be freely soluble in sulphur dioxide, but if quite dry the solution is almost non-conducting, in this respect presenting a great contrast to the corresponding solutions in water.

If the solution contains as an impurity either water or certain organic compounds, the current flows freely with any metal as electrode, the products of electrolysis being hydrogen at the cathode and bromine at the anode. This behaviour is probably to be attributed to interaction between the hydrogen bromide and the second solute resulting in the formation of an oxonium compound, which acts as a good electrolyte.

Oxonium compounds have been investigated by a number of investigators, and especially by Collie and Tickle, Baeyer and Williger, and Archibald and McIntosh.

The last-named workers, for example, have isolated and examined a number of compounds of hydrogen bromide or iodide with compounds such as ether, acetone, and generally with the alcohols, ethers, and ketones.

It has been already noted that hydrogen bromide when dissolved in liquefied sulphur dioxide does not form a highly conducting solution, and experiments have shown that the same may be said of the sulphur dioxide solutions of the following substances:—

|                 |          |               |
|-----------------|----------|---------------|
| Dimethylpyrone, | Acetone, | Benzophenone, |
| Benzaldehyde,   | Ether,   | Water,        |

and *m*-dinitrobenzene, but when small quantities of hydrogen bromide are added to solutions of either of the first six compounds enumerated above, good conducting solutions result; with *m*-dinitrobenzene there is no appreciable change in conductivity.

The compound of dimethylpyrone and hydrogen bromide was isolated and examined by Collie and Tickle; those of acetone and ether with hydrogen bromide were isolated and examined by Archibald and McIntosh, and there can be no doubt that the increase of conductivity in the case of these compounds and in the case of benzophenone and benzaldehyde is due to the formation of these oxonium compounds. If this is granted, we must accept the same explanation for the case of water.

The view that combination of water and hydrogen bromide is an antecedent to conduction is strongly confirmed by the behaviour of mixed solutions of these substances when electrolysed. When water is added to a solution of hydrogen bromide in sulphur dioxide, a small quantity dissolves in the solution, the remainder dissolving some hydrogen bromide and sinking to the bottom as a heavy liquid, which may sometimes crystallise as a white solid which melts below the boiling-point of the sulphur dioxide. This solid is probably one of the hydrates of hydrogen bromide which are known to exist at low temperatures.

When a current is passed through such a saturated solution, small droplets appear on the cathode, increase in size, and fall to the bottom, producing a liquid similar in properties to the solution of hydrogen bromide in water previously mentioned.

If the scheme suggested below, in which water takes part in the conduction, be correct, water should be carried to the cathode, and in a saturated solution be precipitated there. At the same time the anode solution should lose water and become unsaturated. To test this an H-shaped electrolysis vessel was constructed, filled with solution, and an excess of water placed in the anode limb. A stopper was fitted in the tube connecting the two limbs. After passing the current for some time the anode and cathode solutions were separated by means of this stopper and the solutions stirred. The quantity of undissolved water in the anode limb was found to have decreased, that in the cathode limb to have increased.

On account of the many similarities between hydrogen sulphide and water it was considered possible that a solution of hydrogen sulphide in a mixture of sulphur dioxide and hydrogen sulphide might be conducting.

\* A Paper read before the Faraday Society, March 26, 1912.

TABLE II.—Molecular Conductivities.

| Grm.-mols. HBr.          | Of—<br><i>Ether.</i> | Dissolved in x grm. of SO <sub>2</sub> . | Dilution.                 | Specific conductivity.   | Molecular conductivity. |
|--------------------------|----------------------|------------------------------------------|---------------------------|--------------------------|-------------------------|
| 0.0                      | 0.0051               | 9.72                                     | 1.25 × 10 <sup>+3</sup>   | 1.18 × 10 <sup>-4</sup>  | 1.47 × 10 <sup>-1</sup> |
| 0.049                    | 0.0051               | 19.5                                     | 2.5 × 10 <sup>3</sup>     | 1.4 × 10 <sup>-3</sup>   | 3.50                    |
| 0.049                    | 0.0051               | 9.72                                     | 1.25 × 10 <sup>3</sup>    | 2.95 × 10 <sup>-</sup>   | 3.69                    |
| <i>Dimethylpyrone.</i>   |                      |                                          |                           |                          |                         |
| 0.0                      | 0.0011               | 10.17                                    | 6.1 × 10 <sup>+3</sup>    | 1.5 × 10 <sup>-4</sup>   | 9.15 × 10 <sup>-1</sup> |
| 0.011                    | 0.0011               | 10.17                                    | 6.1 × 10 <sup>3</sup>     | 2.8 × 10 <sup>-3</sup>   | 1.74 × 10               |
| 0.011                    | 0.0011               | 19.00                                    | 1.14 × 10 <sup>4</sup>    | 1.47 × 10 <sup>-</sup>   | 1.67 × 10               |
| 0.011                    | 0.0011               | 23.8                                     | 2.02 × 10 <sup>4</sup>    | 0.908 × 10 <sup>-3</sup> | 1.83 × 10               |
| <i>m-Dinitrobenzene.</i> |                      |                                          |                           |                          |                         |
| 0.0                      | 0.00595              | 10.00                                    | 1.100 × 10 <sup>3</sup>   | 1.48 × 10 <sup>-4</sup>  | 1.63 × 10 <sup>-1</sup> |
| 0.025                    | 0.00595              | 10.00                                    | 1.100 × 10 <sup>3</sup>   | 1.50 × 10 <sup>-4</sup>  | 1.65 × 10 <sup>-1</sup> |
| <i>Acetone.</i>          |                      |                                          |                           |                          |                         |
| 0.0                      | 0.007                | 9.5                                      | 9.0 × 10 <sup>2</sup>     | 5.9 × 10 <sup>-5</sup>   | 5.3 × 10 <sup>-3</sup>  |
| 0.016                    | 0.007                | 9.5                                      | 9.0 × 10 <sup>2</sup>     | 1.85 × 10 <sup>-</sup>   | 1.67 × 10               |
| 0.016                    | 0.007                | 20.34                                    | 1.9 × 10 <sup>3</sup>     | 7.46 × 10 <sup>-3</sup>  | 1.43 × 10               |
| <i>Benzophenone.</i>     |                      |                                          |                           |                          |                         |
| 0.00                     | 0.00055              | 10.37                                    | 1.24 × 10 <sup>4</sup>    | 2.0 × 10 <sup>-6</sup>   | 3.72 × 10 <sup>-2</sup> |
| 0.02                     | 0.00055              | 10.37                                    | 1.24 × 10 <sup>4</sup>    | 3.75 × 10 <sup>-4</sup>  | 1.08 × 10               |
| 0.02                     | 0.0033               | 24.67                                    | 4.92 × 10 <sup>3</sup>    | 2.04 × 10 <sup>-3</sup>  | 0.98 × 10               |
| 0.02                     | 0.0033               | 10.37                                    | 2.06 × 10 <sup>3</sup>    | 4.62 × 10 <sup>-3</sup>  | 0.952 × 10              |
| <i>Benzaldehyde.</i>     |                      |                                          |                           |                          |                         |
| 0.00                     | 0.005                | 10.0                                     | 1.31 × 10 <sup>3</sup>    | 1.95 × 10 <sup>-3</sup>  | 2.54 × 10 <sup>-2</sup> |
| 0.025                    | 0.005                | 10.0                                     | 1.31 × 10 <sup>3</sup>    | 4.72 × 10 <sup>-3</sup>  | 6.17                    |
| 0.025                    | 0.005                | 21.9                                     | 2.88 × 10 <sup>3</sup>    | 2.42 × 10 <sup>-3</sup>  | 6.95                    |
| 0.025                    | 0.0283               | 21.9                                     | (5.75 × 10 <sup>3</sup> ) | 1.25 × 10 <sup>-2</sup>  | (7.15)                  |
| <i>Water.</i>            |                      |                                          |                           |                          |                         |
| 0.035                    | 0                    | 9.8                                      | 1.86 × 10 <sup>2</sup>    | 1.5 × 10 <sup>-4</sup>   | 2.8 × 10 <sup>-2</sup>  |
| 0                        | 0.0083               | 9.8                                      | 7.83 × 10 <sup>2</sup>    | 1.5 × 10 <sup>-5</sup>   | —                       |
| 0.035                    | 0.0083               | 9.8                                      | 7.83 × 10 <sup>2</sup>    | 4.2 × 10                 | > 3.3                   |

It was found that sulphur dioxide and hydrogen sulphide did not react in the gaseous state if even moderately dry. Passage rapidly through 5 or 6 cm. of phosphoric oxide dried the gases sufficiently. It was found possible to condense the liquids together at  $-80^{\circ}$  and to prepare solutions of hydrogen sulphide in sulphur dioxide at temperatures up to the boiling-point of that liquid without reaction taking place, in an apparatus dried in a water oven and cooled in air.

A solution so prepared was almost non-conducting, and the addition of hydrogen bromide caused practically no increase in the current.

These results are entirely consistent with the following representation of the reactions that take place:—

1.  $\text{H}_2\text{O} + \text{HBr} \rightleftharpoons \text{H}_3\text{OBr}$ , oxonium bromide.
2.  $\text{H}_3\text{OBr} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Br}^-$ , and during electrolysis.
3.  $2\text{H}_3\text{O}^+ + 2\theta \rightarrow \text{H}_2 + 2\text{H}_2\text{O}$  (at cathode).
4.  $2\text{Br}^- - 2\theta \rightarrow \text{Br}_2$  (at anode).

This series of reactions is extremely interesting as indicating the probability that hydrogen bromide (and inferentially the other halogen hydrides) does not in itself act as an electrolyte, but must first enter into combination with water, or ammonia, or with some compound with which it can form oxonium or ammonium compounds.

Thus when hydrogen bromide dissolves in liquefied ammonia it would be readily conceded that the resulting solution contains ammonium bromide, and when it dissolves in water we must be prepared to recognise the similar formation of oxonium bromide, probably very much dissociated, at the ordinary temperature. The non-formation of a conducting solution when hydrogen bromide is dissolved in the other halogen hydrides or in liquefied sulphur dioxide is probably due, at least in part, to the non-formation of such compounds.

Measurements have been made of the conductivities of sulphur dioxide containing in solution various mixtures of hydrogen bromide and the substances enumerated above, a special apparatus having been made to permit of the preparation of solutions of known strength with carefully dried materials. All the sulphur dioxide used was distilled into the apparatus through a long column of phosphorus pentoxide. The conductivities were determined at a temperature of  $-35^{\circ}\text{C}$ .

The cell constant = 0.059.

The specific conductivity,  $K$ , of pure sulphur dioxide =  $1.5 \times 10$  mhos.

As stated previously, water is not very soluble in a mixture of hydrogen bromide and sulphur dioxide. As time did not permit of determinations of the solubility of the water, the value for the molecular conductivity only represents the minimum possible and is really too low, excess of water having been added.

The results of the measurements are collected in Table II., which shows the number of grm. molecules of hydrogen bromide, of water, or other solute, or of both, which are dissolved in the stated weight of sulphur dioxide.

The fourth column contains the dilution of the solution expressed as the number of cc. of solution containing 1 grm. molecule of dissolved substance.

The fifth column contains the values of the specific conductivities of the various solutions, and the molecular conductivities are given in the last column.

The molecular conductivities which are given in the case of the mixed solutions are those of the water or other organic solvent, with the exception of the most concentrated solution of benzaldehyde, the concentration of which is greater than that of the hydrogen bromide. In this case the figures in brackets refer to the volume con-



taining 1 grm. mol. of hydrogen bromide and the corresponding molecular conductivity.

TABLE III.—Some Molecular Conductivities Compared.

1. KCl in H<sub>2</sub>O, 125.
2. HBr in SO<sub>2</sub>, 0.0405.
3. Acetone in SO<sub>2</sub>, 0.0053.
4. HBr Acetone in SO<sub>2</sub>, 16.7.
5. HBr Ether in SO<sub>2</sub>, 3.7.
6. HBr Dimethylpyrone in SO<sub>2</sub>, 17.4.
7. HBr Benzaldehyde, 6.95.
8. HBr Benzophenone, 10.8.
9. HBrH<sub>2</sub>O in SO<sub>2</sub>, >3.3.

In order to convey a clear idea of the actual magnitude of the conductivities of these solutions a few molecular conductivities have been collected in Table III. It will be seen that the molecular conductivity of a mixture of water and hydrogen bromide in sulphur dioxide is of the same order of magnitude as that of a 1 per cent solution of acetic acid in water (3.5), while the specific conductivity ( $4 \times 10^{-3}$ ) is several times greater than that of the acetic acid solution at 18° ( $5.8 \times 10^{-4}$ ).

In all cases but one the quantity of hydrogen bromide is considerably in excess of that required for combination with the other solute, and the dilution has been calculated on the assumption that practically all of the water or organic solute has combined with the hydrogen bromide.

The figures for meta dinitrobenzene indicate that no combination of the two compounds is brought about. It has been found that the conductivity of certain solutions varies with time, and this variation is well shown by the following figures, Table IV., which refer to experiments with water, with ether, and with acetone.

TABLE IV.—Variation of Molecular Conductivity with Time.

| Solution containing                                               | Time in mins. after mixing. | Mol. conductivity. |
|-------------------------------------------------------------------|-----------------------------|--------------------|
| H <sub>2</sub> O 0.0083 grm. mol. . . . .                         | 0.0                         | 3.31               |
| HBr 0.035 grm. mol. in 6.5 cc. }<br>of SO <sub>2</sub> . . . . .  | 780                         | 2.72               |
| Ether 0.0051 grm. mol. . . . .                                    | 0                           | 3.68               |
| HBr 0.049 grm. mol. in 6.4 cc. }<br>of SO <sub>2</sub> . . . . .  | 1250                        | 4.56               |
| Acetone 0.007 grm. mol. . . . .                                   | 0                           | 14.8               |
| HBr 0.010 grm. mol. in 6.23 cc. }<br>of SO <sub>2</sub> . . . . . | 900                         | 16.5               |
| Acetone 0.007 grm. mol. . . . .                                   | 0                           | 14.2               |
| HBr 0.016 grm. mol. in 13.4 cc. }<br>of SO <sub>2</sub> . . . . . | 1900                        | 17.3               |

When a water mixture was allowed to stand for several hours a heavy oily liquid appeared at the bottom. The fall in conductivity might be attributed to the slow formation of this substance, which in general properties corresponded with sulphur bromide. It is hoped to investigate the nature of the substance more fully at a later date.

The rise in molecular conductivity which occurs with the other substances is consistent with the supposition that the velocity of the formation of the oxonium compound is not instantaneous, the conductivity rising with the increase in concentration of the compound.

#### Electrolysis of Solutions of Ether and HBr in SO<sub>2</sub>.

With ether solutions current flowed freely, but at the start of the experiment very little hydrogen was evolved. After the current had passed for some time (an hour or two) much more gas could be collected. Quantities up to about two-thirds of the theoretical amount were collected from solutions which had previously been electrolysed for some time.

With water solutions more gas was evolved at the commencement of the electrolysis, approximately half the

theoretical volume, but this quantity did not increase with continual passage of the current.

The fact that hydrogen is not evolved in theoretical volume may be explained by the suggestion that some is used up in the formation of reduction products.

In view of its possible bearing on the nature of the hydrogen ion and on the general theory of electrolysis, it is hoped to extend that portion of the work dealing with the conductivity and electrolysis of hydrogen bromide solutions at a later date.

#### Electrolysis of Potassium Mercury Iodide.

Qualitative attempts were made to electrolyse solutions of certain double salts, as, for example, the double compound of potassium and mercury iodides. It was found that this compound behaved very similarly to potassium iodide; a deposit containing sulphur being formed on the cathode, and the current falling very rapidly to the usual small value. In one experiment, in which the materials had not been carefully dried, it was found that mercury was deposited as a film on a strip of copper immersed in the solution, but when the experiment was repeated with carefully dried materials no such effect could be produced.

#### Electrode Potentials of the Metals.

The programme mapped out for the determination of the electrode potentials was as follows:—

1. To determine the electrode potentials of metals when immersed in saturated solutions of their salts.
2. To determine the solubility of these various salts, using for the purpose the microbalance recently described by Steele and Grant (*Proc. Roy. Soc.*, 1909, A, lxxiii., 580).
3. To determine the conductivities of extremely dilute solutions of these salts, and so to ascertain the ionic concentrations of the various metallic ions.

From the data thus obtained it should be possible to calculate the normal electrode potentials of the metals when dissolved in a solvent such as sulphur dioxide, which contains no hydrogen, and to compare the values thus determined with those obtained in aqueous solutions.

Owing to the removal of one of us from Melbourne to Brisbane, and the consequent temporary loss of facilities for experimental work, this programme has been interrupted, and the only part actually carried out is the measurement of the electrode potential of metals immersed in saturated solutions of their salts.

The choice of metals and salts was limited in the first place by the fact that the only freely soluble metallic salts are the bromides and iodides of the alkali metals, and that these are not capable of being used for electrodes on account of their rapid tarnishing in an atmosphere of dry sulphur dioxide.

On the other hand, the salts of other metals being extremely insoluble, cells prepared with saturated solutions of these salts have an extraordinarily small capacity. As a consequence of this, it was found to be impossible to determine the e.m.f. of these combinations by the usual potentiometer method, since the minute amount of current taken out of the cells during the measurement immediately lowered the e.m.f. to zero.

The measurements were therefore carried out with a quadrant electrometer, one pair of quadrants being earthed and the other connected with one electrode of the cell, the other electrode being earthed. The electrometer was one of very small capacity, and it was found that no polarisation was produced in the cell when its e.m.f. was measured by this method. It was not found possible to use the ordinary dipping electrode vessels, and therefore an apparatus was designed for the measurements. This apparatus consisted of two electrode vessels immersed in a wide test-tube. One of these vessels is shown in Fig. 2. It consists of an H-shaped tube, one limb of which, A, is closed at the bottom, the other, B, being open. The open limb is provided with a ground-in hollow glass stopper, C, with a hole drilled in it opposite the connecting tube, D, and by rotating this stopper the solution contained in the closed limb could

be brought into communication with the liquid in the wide test-tube E.

The two electrode vessels were fitted in a rubber cork, F, which in its turn fitted the test-tube, and the whole could be immersed in a Dewar flask containing liquefied ammonia.

In carrying out an experiment, the electrodes, G, which were composed of a wire of the metal under investigation, were placed in the closed limb of the H-tube, a small portion of the selected salt of the metal having been first placed in the same limb. The upper end of the tube containing the wire was then sealed with sealing-wax and the

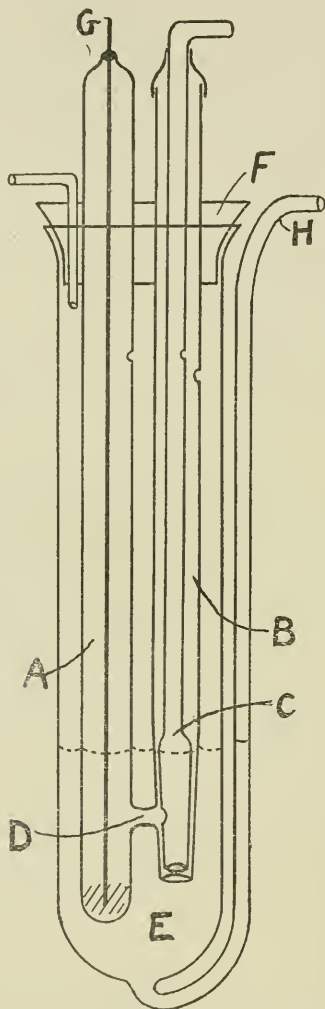


FIG. 2.

apparatus exhausted and dried. When it was judged that the whole apparatus was thoroughly dry, it was immersed in a bath of liquefied ammonia, the electrode vessels placed in communication with the test-tube by turning the stopper, and sulphur dioxide distilled into the apparatus through H. The sulphur dioxide filled the test-tube to the required level and overflowed into the electrode vessels, forming there after the lapse of a few hours a saturated solution of the salt in question. It was usually found that the film of sulphur dioxide surrounding the stopper was sufficiently conducting to allow of readings being taken without polarisation effect being observed.

The materials employed were from various sources, and were subjected to various methods of purification, with the object of testing whether the effects measured were due to the presence of minute quantities of impurities.

A sufficient number of measurements have been made to indicate that each metal has a definite electrode potential when immersed in liquefied sulphur dioxide, and that the magnitude of the potential is affected by the concentration of the metallic ion in solution in the same manner and in the same direction as it is in aqueous solution.

The measurements that are described were made at a temperature of  $-35^{\circ}\text{C}$ . The deflections of the electrometer were standardised by means of a standard Clark cell. The standard electrode employed was one of mercury, covered with a layer of purified mercurous chloride, made into a paste with liquefied sulphur dioxide.

The following measurements of the e.m.f. of a typical cell are given as an example of the degree of constancy of e.m.f. which can be obtained with the extremely dilute solution which it was necessary to employ.

*Cell Constancy of  $\text{Hg}/\text{HgCl}$  in  $\text{SO}_2/\text{SO}_2/\text{PbCl}_2$  in  $\text{SO}_2/\text{Pb}$ .*

| Time of measurement. |    | E.M.F. |    |    |    |    |       |
|----------------------|----|--------|----|----|----|----|-------|
| H. M.                |    |        |    |    |    |    |       |
| 0                    | 0  | ..     | .. | .. | .. | .. | 0.40  |
| 1                    | 45 | ..     | .. | .. | .. | .. | 0.427 |
| 3                    | 15 | ..     | .. | .. | .. | .. | 0.430 |
| 5                    | 0  | ..     | .. | .. | .. | .. | 0.437 |
| 7                    | 30 | ..     | .. | .. | .. | .. | 0.430 |
| 8                    | 45 | ..     | .. | .. | .. | .. | 0.433 |

A.  $\text{Pb}/\text{PbCl}_2/\text{HgCl}/\text{Hg}$ . Mercury electrode negative.

1. E.m.f. = 0.435 volt.
2. Same cell, but freshly prepared and purified materials.  
E.m.f. = 0.435 volt.

B.  $\text{Zn}/\text{ZnBr}_2/\text{HgCl}/\text{Hg}$ . Mercury electrode negative.

1. Pure zinc cast into rod.  
Zinc bromide distilled.  
E.m.f. 0.38 to 0.40 volt.
2. Zinc bromide re-distilled.  
E.m.f. 0.37 to 0.40 volt.

C.  $\text{Cd}/\text{CdI}_2/\text{HgCl}/\text{Hg}$ .

1. Cd metal electrolytic, Schuchardt, cadmium iodide re-crystallised.  
E.m.f. 0.42 to 0.445 volt.
2. Freshly prepared and treated material from the same stock.  
E.m.f. 0.42 to 0.43 volt.

Addition of potassium iodide and of tetramethylammonium iodide to the solution surrounding the cadmium iodide instantly altered the e.m.f., and in all cases tested the e.m.f. was sensitive to the addition of any salt having an anion common to the added and dissolved salt.

*Summary.*

In the foregoing pages experiments are described which were designed to ascertain the mechanism of electrolysis in liquefied sulphur dioxide.

1. It has been shown that during the electrolysis of solutions of potassium or sodium iodides, tetramethylammonium iodide, trimethylsulphonium iodide, sulphur is deposited on the cathode, and that a sulphite is simultaneously formed.

2. That, at the anode, changes occur which are analogous to those occurring in aqueous solution. For instance, bromine and iodine are liberated from solutions of bromides and iodides.

3. That anodes of zinc and iron are attacked and pass into solution as complex iodides when iodides are electrolysed.

4. Evidence has been adduced to show that water and hydrogen bromide unite to form an oxonium compound which is electrolytic in character, and this evidence has



been strengthened by comparison with the behaviour of several well known oxonium compounds.

5. A few electrode potentials of metals immersed in saturated solution of their salts have been measured.

In conclusion, the authors wish to express their thanks to the Government Grant Committee of the Royal Society for a grant made to one of us by means of which a large portion of the expense of the work has been met. We also wish to express our thanks to Messrs. Felton, Grimwade, and Co. for their kindness in presenting us with large quantities of liquefied ammonia.

Chemical Laboratories,  
The University of Melbourne.

# THE PHENOMENON OF OCCLUSION IN PRECIPITATES OF BARIUM SULPHATE, AND ITS RELATION TO THE EXACT DETERMINATION OF SULPHATE.\*

By JOHN JOHNSTON and L. H. ADAMS.

(Continued from p. 165).

## Effect of Digesting the Precipitate with Acid.

PRECIPITATES were made in the usual way from solutions containing  $\text{Na}_2\text{SO}_4 + 5$  grms.  $\text{NaCl} + 0.2$  cc. 20 per cent  $\text{HCl}$ ; after standing eighteen hours, the supernatant liquid was decanted off, and 50 cc. 20 per cent hydrochloric acid were poured over the precipitate. After standing thus for twenty-four hours, the occlusion was determined. The mean result found was 0.43 per cent, as compared with 0.70 per cent, the amount of occlusion after contact with the supernatant liquid for a similar interval. In other experiments, the barium sulphate was precipitated from neutral solution (containing 5 grms. sodium chloride), and immediately after precipitation (a) 60 cc. 40 per cent hydrochloric acid, and (b) 50 cc. concentrated nitric acid were added. The amount of occlusion after eighteen hours' contact with these solutions was (a) 0.32 per cent, (b) 0.44 per cent; whereas, without the acid, the amount is 0.90 per cent.

There is no doubt that the greatly increased rate of diminution of occlusion in presence of these acids is directly due to the increased rate of re-crystallisation of the precipitate, which is, in turn, a consequence of the notably greater solubility of barium sulphate in hydrochloric and nitric acids (Banthisch, *Journ. Prakt. Chem.*, 1884, xxix., 54; through Seidell's "Solubilities of Inorganic and Organic Substances"). The amount of occlusion is thus greatly reduced by contact with a solution containing 60 cc. 40 per cent hydrochloric acid added after precipitation; but not so much as if the same amount of acid is present in the solution before precipitation. Under these conditions we found only 0.16 per cent, and observed that the amount was practically independent of the time of standing, as might be expected from the fact that precipitates formed in this way are quite coarse-grained, and to that degree less easily purified.

## General Discussion of Results.

In the preceding it has been shown that precipitates of barium sulphate carry down some, or all, of the other salts present in the solution; that the amount of the occlusion varies (1) with the concentrations of the salts; (2) with the rate of precipitation, solubility of the barium sulphate in the supernatant liquid, and with the age of the precipitate at filtration; in a word, it varies with the fineness of the precipitate, which in turn is controlled by the above three factors. Proof of this statement is afforded in a series of papers by P. P. von Veimarn (*Zeit. Chem. Ind. Kolloide*, 2, 3, *passim*), which deal with the size and appearance of the particles of barium sulphate, formed by

mixing solutions of barium thiocyanate and manganous sulphate, the concentration of which varied between wide limits. His conclusions have a direct bearing on the problem considered in the present paper, and may therefore be briefly recapitulated.

Von Veimarn's general thesis is that amorphous bodies are not precipitated as such from solution; i.e., that the particles of so-called amorphous precipitates are always crystalline, and consequently that the differences between the various modifications of the solid state are in degree and not in kind, in the state of aggregation of the particles and not in differences of structure between the particles themselves. Starting from this point of view, he enunciates the theorem that, if a substance A (e.g.,  $\text{BaSO}_4$ ) is formed by the interaction of two solutions B and C ( $\text{Ba}(\text{CNS})_2$  and  $\text{MnSO}_4$ ), the form in which it appears depends upon the concentration of the ions  $\text{Ba}^{++}$  and  $\text{SO}_4^{--}$  in the mixture of B and C, relative to their concentrations in the solution which is saturated with  $\text{BaSO}_4$  under the conditions of experiment.

To demonstrate this, he mixed a solution of barium thiocyanate with manganous sulphate of the same concentration (which ranged from about 0.0001 N to about 7 N), and examined the precipitates at frequent intervals. His observations led him to divide the whole range of concentrations into five regions, each of which, of course, merges into the adjacent regions. The dilutions given are those of each solution before mixing; their reciprocals therefore represent approximately (except in the very strongest solutions) the equivalent concentration of  $\text{Ba}^{++}$  and of  $\text{SO}_4^{--}$  at the moment of precipitation.

1. At dilutions greater than 7000, the precipitate does not separate at all.

2. At dilutions between 7000 and 600, one obtains in the course of time recognisable crystals by the slow transformation of the form originally precipitated, which is that usually known as amorphous. These "amorphous" grains, however, equally with the finest grains obtainable by mechanical means, have the power of inhibiting supersaturation. The general behaviour within this region is indicated by the following table:—

| Dilution approx. | Distinct opalescence appears in— | The bulk of the precipitate settles in— | Remarks.                                                                                                                         |
|------------------|----------------------------------|-----------------------------------------|----------------------------------------------------------------------------------------------------------------------------------|
| 5000             | —                                | 1 month                                 |                                                                                                                                  |
| 3000             | 6—8 hours                        | 24 hours                                | Initially an ultra-microscopic suspension; transformed after six months into good crystals about 0.001 cm. long.                 |
| 2000             | 2—3 hours                        | 10—12 hours                             | Initially fine-grained spherical aggregates, transformed after six months into good crystals of smaller size than the preceding. |
| 1000             | 3—5 mins.                        | 2—3 hours                               |                                                                                                                                  |
| 600              | A few secs.                      | $\frac{1}{2}$ —1 hour                   |                                                                                                                                  |

Further experiments at the dilution 2000 showed that the process of re-crystallisation requires several months, while the direct crystallisation requires but a few hours at room temperature, without shaking. On the other hand, supersaturation is removed within a few minutes, the length of this interval depending largely on the slowness of diffusion in the neighbourhood of the crystal grains.

3. At dilutions between 600 and 1 the number of good crystals diminishes, and the formation of skeletons and needles increases with increase in concentration. At 200 the skeletons may be about 0.0005 cm. in length, while the

size of the needles varies from perhaps  $10\ \mu$  down to the smallest points visible in the microscope. At a dilution of 10 the precipitate consists entirely of needles; about 1 the formation of amorphous precipitate begins.

4. At dilutions between 1 and 0.1 one obtains initially jelly-like amorphous precipitates, which may be differentiated into aggregates microscopically; these quickly become turbid, and change into voluminous fine-grained precipitates.

5. At the greatest concentrations, jellies are obtained, the particles of which initially cannot be differentiated, even with the ultramicroscope; they remain transparent for several hours, but in about twenty-four hours are transformed into a plastic mass. This does not change its structure in many months when preserved under water at low temperature; but in boiling water a considerable part of it re-crystallises in three weeks, while in a hot concentrated solution of hydrochloric acid, complete re-crystallisation takes place in a few days.

From the above observations von Veimarn shows in two ways that the "amorphous" precipitates are composed of crystalline material; first, because with increasing concentration—which is equivalent to decreasing relative amounts of  $\text{Ba}^{++}$  and  $\text{SO}_4^{--}$  in the solution—there is a progressive diminution in the size of the crystals, but no sudden change to amorphous; and, secondly, because all precipitates are capable of re-crystallisation. The process of re-crystallisation consists in the inhibition by the larger crystals of the supersaturation (with respect to them) of the solutions formed by the greater solubility of the smaller crystals (see G. A. Hulett, *Zeit. Phys. Chem.*, 1901, xxxvii., 396). The slowness of this process is plausible, when account is taken of the degree of supersaturation and of the very small absolute amount of material. Naturally, too, the finest grained material may require considerable time to grow to recognisable crystals.

Von Veimarn's papers have been summarised above rather fully because they show that the fineness of the precipitate depends upon the concentration of  $\text{Ba}^{++}$  and  $\text{SO}_4^{--}$  relative to that of a saturated solution of barium sulphate in the particular medium; or, in other words, the fineness of grain is conditioned by the degree of supersaturation of the barium sulphate in the solution.

(NOTE.—This is equivalent to the statement that diminution of the solubility causes an increase in the number of centres of crystallisation. It may be noted that the number of centres increases also with the viscosity of the medium; for increased viscosity decreases the motion of the centres, and therefore increases their number, since the total amount of substance precipitated remains the same).

This is confirmed by other observations; thus, whereas von Veimarn obtained in concentrated solutions particles about  $5\ \mu$  in diameter, we were able to obtain crystals 1 to 2 mm. long in diffusion experiments, in which the degree of supersaturation was kept very small, and crystals up to 4 cm. in length have been found in the Teplitz springs in which barium could not be detected by ordinary analytical methods (F. Becke, *Min. Petrog. Mitt.*, 1883, v., 82).

Since the size of the crystal particles depends upon the degree of supersaturation, it follows that the degree of fineness of the particles is increased by a rapid addition of the precipitant; is diminished by precipitating in a medium in which barium sulphate is more soluble; and is further diminished, when the precipitate remains in contact with a medium in which it is soluble, by the process of re-crystallisation, the rate of which depends upon this solubility. Now these are precisely the conditions which affect the occlusion when the precipitates are made from identical solutions. We are therefore justified in concluding that this occlusion is a phenomenon of absorption at the surface of the grains of the precipitate, and that its amount depends upon (a) the composition of the original solution, and (b) the initial fineness of the precipitate and the amount of re-crystallisation which has taken place.

This explanation, besides accounting for our own results,

also accords with those of Richards and Parker (*Proc. Am. Acad.*, 1898, xxxi., 67; *Zeit. Anorg. Chem.*, 1895, viii., 413), and of Hulett and Duschak (*Zeit. Anorg. Chem.*, 1904, xl., 196), who studied the precipitates obtained by mixing solutions of barium chloride and sulphuric acid; moreover, it does not conflict with any reliable experimental evidence with which we are acquainted.

These considerations might be applied to elucidate and correlate the enormous number of mineralogical papers dealing with the composition and crystal habit of natural and artificial barite. This would, however, lead too far at present. It may suffice to mention, perhaps, the latest of these, a paper by Hilda Gerhart (*Min. Petrog. Mitt.*, 1910, xxix., 185); crystals of barite were made by the action of various solutions on barium chloride through a layer of gelatinous silicic acid, and it was found that alum and nitric acid exert the greatest influence in modifying the crystal habit. Now, these substances are absorbed to a considerable extent by barium sulphate. This renders it plausible that one factor in the modification of crystal habit is the occlusion by the growing crystal of foreign substances from the supernatant liquid.

#### The Exact Determination of Sulphate.

By the method given in the previous paper (Allen and Johnson, *loc. cit.*), accurate determinations of sulphate are possible only if three corrections are applied, one of which at least—the correction for "volatility"—is somewhat troublesome to determine. Series of experiments were therefore made in order to find out if it be possible by the application of the principles stated above to devise a general method for the accurate determination of sulphate, in which only slight and easily determined corrections should be necessary. This endeavour to find a generally applicable simple method has not been altogether successful; it was found possible to obtain correct results in some particular instances, but in general these were due to a compensation of errors, all of which were small.

In actual analytical work, the only readily variable effective conditions are the acidity of the original solution and of the supernatant liquid, and to some extent the rate of addition of the precipitant; accordingly we attempted by variation of these conditions to obtain coarse-grained precipitates, and thereby correct results. The attempts, which were made on solutions of sodium sulphate containing, in general, sodium chloride, are briefly described below, and the reasons of their failure are indicated. The manipulation and methods used, e.g., in treating the precipitate, are identical with those described in the previous paper; the total volume of the solution was always 350 cc., and the time of precipitation about four minutes, except where it is expressly stated otherwise.

#### (a) Precipitation in Strongly Acid Solution.

When the original solution is strongly acid, the solubility becomes important, as it amounts to over 30 mgrms. in the most acid solutions used (50 cc. concentrated 40 per cent hydrochloric acid in 350 cc. solution). The solubility was taken into account: (a) by evaporating the filtrate to dryness (this is best done in platinum vessels), taking up with a little water, filtering, weighing separately, and adding this to the weight of the main portion of the precipitate; (b) by evaporating the whole solution (with the precipitate) to dryness immediately after precipitation (this is best done in platinum vessels), taking up with water, filtering, washing, and igniting as usual. The results of both methods are identical; they are presented in Table VI., in the column headed " $\text{BaSO}_4$  found." In Table VI. is also given the amount of occlusion wherever it was determined, together with the correction corresponding to the assumption that all of the sodium sulphate found was originally present as  $\text{NaHSO}_4$ , the reaction  $2\text{NaHSO}_4 = \text{Na}_2\text{SO}_4 + \text{H}_2\text{SO}_4$  taking place on ignition of the precipitate, with a consequent loss of half of the total quantity of  $\text{SO}_3$  occluded. For such acid solutions this



TABLE VI.—Sulphate Determinations in Strongly Acid Solutions.

| Original solution contained— |                  | BaSO <sub>4</sub> . |        | Deficit.<br>(uncorr.). | Occlusion. |                 | Error (corrected<br>for occlusion). (b) |
|------------------------------|------------------|---------------------|--------|------------------------|------------|-----------------|-----------------------------------------|
| NaCl.                        | 40 per cent HCl. | Calculated.         | Found. |                        | Found.     | Correction. (a) |                                         |
| Grms.                        | Cc.              | Grms.               | Grms.  | Grms.                  | Mgrms.     | Mgrms.          | Per cent.                               |
| 0                            | 25               | 1.9955              | 1.9882 | 7.3                    | 4.4        | 6.0             | -0.06                                   |
| 5                            | 25               | 1.9938              | 1.9810 | 12.8                   | —          | —               | —                                       |
| 5                            | 50               | 1.9894              | 1.9902 | -0.8                   | 3.2        | 4.4             | 0.26                                    |
| 5                            | 50               | 1.9965              | 1.9967 | -0.2                   | —          | 4.4             | 0.23                                    |
| 5                            | 50               | 2.0022              | 2.0014 | 0.8                    | —          | 4.4             | 0.18                                    |
| 10                           | 50               | 1.9995              | 1.9812 | 9.3                    | 4.6        | 6.4             | -0.14                                   |
| 0                            | 50 (c)           | 1.9750              | 1.9811 | -6.1                   | 2.1        | 3.0             | 0.45                                    |
| 5                            | 50 (c)           | 2.0076              | 2.0152 | -7.6                   | 1.4        | 2.0             | 0.48                                    |

(a) This is best done in platinum vessels.

(b) On the assumption that the sulphate occluded is wholly NaHSO<sub>4</sub>.

(c) In these two experiments precipitation was rapid—in about ten seconds; they are therefore not strictly comparable with the others.

assumption must be more nearly correct than the simpler one made previously—namely, that the correction is given by  $(\text{BaSO}_4 - \text{Na}_2\text{SO}_4)/\text{Na}_2\text{SO}_4$ ; on the newer assumption the correction is exactly twice as great as this.

The numbers in the last column represent the percentage error of the determination, after the above correction has been applied. It is evident that this error is nearly constant for any given original solution and tends to be positive; this is easily accounted for by the fact that the precipitates all contained a trace of chloride, the amount of which was not determined quantitatively, and has not been allowed for. The influence of the chloride is especially marked in the last two experiments, in which the precipitation was made rapidly—in about ten seconds; this condition is, conformably with what we had previously found by actual determinations of the chloride, favourable to increased occlusion of chloride. Moreover, the concentration of hydrochloric acid would decrease greatly the ionisation of the barium chloride, and hence tend to increase the occlusion of the latter, other things being equal; in somewhat stronger acid solution, precipitation of barium chloride might even occur. (The solubility of barium chloride is enormously diminished by hydrochloric acid; for quantitative data see Engel, *Ann. Chim. Phys.*, 1888, [6], xiii., 371.) It is evident, however, from Table VI. that, by making slow precipitations in presence of much free hydrochloric acid (50 cc. 40 per cent in 350 cc. original solution) and taking the solubility into account, fair results are obtained, especially with solutions containing 5 grms. sodium chloride—a quantity such as is very commonly present in actual work. Correcting for occlusion tends to make the results high, because the precipitates are also contaminated with barium chloride, which is not allowed for in that correction. Incidentally it may be mentioned that the manipulation of the precipitates obtained from acid solutions is much easier and more rapid, by reason of their coarseness of grain.

(To be continued).

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

Ordinary Meeting, March 28th, 1912.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"Confusion Test for Colour Blindness." By Dr. G. J. BURCH, F.R.S.

A sheet of perforated zinc is fixed in the focal plane of a convex lens of about eight diopeters, through which the observer looks. On a card 6 inches or so farther off is painted a design in confusion colours, e.g., red and blue letters on a dark green ground. The red-blind can distinguish the blue letters but not the red, though these are far more conspicuous to the normal.

The letters being out of focus, brush marks are invisible, and new designs can be easily drawn. Other colours are:—Geranium red with French grey; emerald green with yellow ochre; lilac with blue—this last being a test also for the green-blind.

The colours used were matched by the late Lieut.-Col. Scott, who was red-blind.

"Systematic Position of the Spirochaets." By CLIFFORD DOBELL.

"Influence of Selection and Assortative Mating on the Ancestral and Fraternal Correlations of a Mendelian Population." By E. C. SNOW, M.A.

Using the simple hypothesis of Mendel, the author investigates by analytical methods the numerical effect on the ancestral and fraternal correlations of dealing with samples (a) which are not true random samples of the general population and which mate with no sexual selection, (b) which are perfectly random samples of the general population but mate with certain intensity of assortative mating, (c) which are selected samples showing assortative mating. The general effect is the same for somatic characters as for gametic; in the case of (a) the correlations are found to be reduced, and in the case of (b) to be increased throughout. For (c) the two effects are superimposed, but it is found that the decreasing tendency caused by dealing with a selected sample predominates over the increasing tendency exerted by the assortative mating in cases in which the intensities of the selection and assortative mating are of the orders of those actually experienced.

The general numerical results agree fairly well with the values which have previously been reached by other methods, but the investigation in no way diminishes the difficulties in the way of reconciling the "regressions" which follow from Mendelism for certain characters (e.g., coat-colour in mice) with those actually found in statistical researches. So far as numerical results are concerned, the investigation supports the view that the Mendelian hypo.

Royal Institution.—On Tuesday next, April 16, at 3 o'clock, Dr. Edmund Gosse begins a course of two lectures at the Royal Institution on "Algernon Charles Swinburne, his Early Life and Work"; on Thursday, April 18, Prof. A. W. Crossley delivers the first of two lectures on "Synthetic Ammonia and Nitric Acid from the Atmosphere"; and on Saturday, April 20, Mr. Reginald Blomfield commences a course of three lectures on "The Architecture of the Renaissance in France, 1494—1661." The Friday Evening Discourse on April 19 will be delivered by Mr. Alan A. Campbell Swinton on "Electricity Supply—Past, Present, and Future"; and on April 26 by Sir George H. Darwin on "Sir William Herschel." In addition to the Friday Evening arrangements already announced, the discourse on May 24 will be delivered by Mr. A. D. Hall on "Recent Advances in Scientific Agriculture—the Fertility of the Soil"; and on June 14 by Mr. A. H. Savage Landor on his recent journey through unknown parts of South America.

thesis can be employed to give confirmation to results which have at first sight appeared paradoxical (*e.g.*, the closeness of the resemblance between first cousins) and to give a rough indication of the probable results in cases for which actual statistical data are inadequate (*e.g.*, the inquiry into the effects on the offspring of inbreeding of various degrees).

"Human Electrocardiogram; a Preliminary Investigation of Young Male Adults, to form a Basis for Pathological Study." By T. LEWIS and M. D. D. GILDER.

"Production of Variation in the Physiological Activity of *Bacillus coli* by the use of Malachite-green." By C. REVIS.

*Bacillus coli* can be trained to grow in nutrient broth containing malachite-green. By gradually increasing the percentage of the malachite-green the organisms will develop readily in presence of 0.10 per cent. In most cases the organism at the same time undergoes a profound change in its physiological activity towards sugars and polyhydric alcohols, acid only being produced in certain of these, from which the organism originally produced both acid and gas, the power of gas formation being permanently lost. In one instance this change in physiological activity was accompanied by equally profound morphological and cultural changes, the resultant organism being quite different to that from which it had been produced. The change brought about by malachite-green indicates a connection between the typhoid and *coli* groups and the possibility of development of organisms of the one into those of the other.

"Notes on some Flagellate Infections found in certain Hemiptera in Uganda." By MURIEL ROBERTSON.

"Notes on certain Aspects of the Development of *T. gambiense* in *Glossina palpalis*." By MURIEL ROBERTSON.

"Antelope and their Relation to Trypanosomiasis." By Dr. H. L. DUKE.

"Nature of Pancreatic Diabetes (Preliminary Communication)." By F. P. KNOWLTON and Prof. E. H. STARLING, F.R.S.

## PHYSICAL SOCIETY.

Ordinary Meeting, February 23rd, 1912.

Prof. A. SCHUSTER, F.R.S., President, in the Chair.

A PAPER ON "A Balance Method for the Accurate Comparison of Quantities of Radium and some of its Applications," by Prof. E. RUTHERFORD and Mr. J. CHADWICK, was read by Prof. RUTHERFORD.

A balance method is described for accurately comparing quantities of radium by their  $\gamma$ -radiation, in which the ionisation due to the  $\gamma$ -rays is balanced against the constant ionisation due to uranium oxide. By observing the distance of the radium preparation from the ionisation chamber when a balance is obtained, the relative  $\gamma$ -ray activities of the two preparations can be determined with an accuracy of at least 1 part in 400. A method of calibration is given, and the corrections necessary to deduce the quantities of radium present are considered.

Calculations are given showing the correction required to determine a quantity of emanation by comparison of its  $\gamma$ -ray activity with that due to a radium standard.

The balance method was employed to determine the period of transformation of the radium emanation. The half value period was found to be 3.854 days. It was found experimentally that the  $\gamma$ -ray activity due to the radium emanation and its products reaches a maximum 255 minutes after the introduction of the emanation into a sealed tube. Calculations showed that under the experimental conditions the theoretical maximum should be reached after 255 minutes.

It was found that the  $\gamma$ -ray activity of a radium preparation was not appreciably altered by exposure in a strong magnetic field.

A paper on "The Absorption of  $\gamma$ -rays by Gases and Light Substances," by Mr. J. CHADWICK, was read by Prof. RUTHERFORD.

The absorption coefficients of air, carbon dioxide, and hydrogen for the  $\gamma$ -rays from radium have been measured after the rays have traversed 3 mm. and 1 cm. of lead. The gases were contained in an iron cylinder, and were under considerable pressure. The values found for the absorption coefficients are, at normal temperature and pressure, 0.000062, 0.000102, and 0.000042 (cm.)<sup>-1</sup> for air, carbon dioxide, and hydrogen respectively, the thickness of lead being 3 mm. When the thickness of lead is 1 cm. the absorption coefficients of air and carbon dioxide are 0.000059, 0.000092 (cm.)<sup>-1</sup> respectively.

The absorption coefficient of air has also been determined by using liquid air. The absorption coefficients found in this way are in good agreement with the values found for air under pressure, showing that the absorption of  $\gamma$ -rays is not affected by temperature.

The absorption coefficients of a number of light substances have also been found.

The two preceding papers were discussed together.

Prof. H. L. CALLENDAR fully appreciated the difficulty of accurately comparing quantities of radium by the electroscopic method. He had a year or two ago made some measurements of the heat given out by radium, and found that with only 2 or 3 mgrms. the heat could be measured to 1 part in 1000.

Dr. J. H. VINCENT commented on the value of the new method for the accurate comparison of quantities of radium. It was also valuable to have further tables of the absorption of  $\gamma$ -rays by different substances.

Dr. S. RUSS asked whether Prof. Rutherford attributed the diminution of the coefficient of absorption for  $\gamma$ -rays with increase of distance traversed to the lack of homogeneity of the rays themselves.

Dr. G. W. C. KAYE remarked that the Röntgen Ray Society several years ago considered the question of a Radium Standard. He hoped that when prepared the standard would be placed so that other workers could standardise their radium by it.

Prof. A. W. BICKERTON asked whether it was now regarded as finally established that the  $\alpha$ -rays are nothing but helium.

Prof. C. H. LEES asked concerning the preparation of the Primary Standard.

The PRESIDENT remarked on the advantages of being able to get accurate quantitative measurements in any science. The early workers on vacuum tube discharges experienced the same difficulty as the early workers on radio-activity in getting accurate quantitative measurements of the effects. He also asked how the thickness of the tube containing the radium was found.

Prof. E. RUTHERFORD, in reply, stated that the thickness of the tube, if not measured before putting the radium into it, could be found approximately by weighing and measuring. Since the absorption it caused in the  $\gamma$ -rays was in general less than 1 per cent its thickness need only be known approximately. With regard to the homogeneity of the  $\gamma$ -rays, they were probably as complex as any radiation could very well be. It had been found that radium B gives out  $\beta$ -rays of 28 or more different velocities, and Messrs. Moseley and Makower had recently found that it also gave out different kinds of  $\gamma$ -rays. It was remarkable that the absorption followed an exponential law over such a wide range, but there might be some homogeneity in the rays after the very soft ones were absorbed. We do not know what is happening in the material when the rays are being absorbed.

The Primary Standard of Radium would be purified by chemical processes as much as possible, and then weighed and sealed in a tube, and only future generations would be able to determine how pure it was. The chief trouble in purification was with meso-thorium, which could not be separated from radium by chemical means. Fortunately the Joachimsthal granitic deposits from which the primary



and the duplicate standards would be prepared were practically free from thorium.

There could, he thought, be no doubt now that the  $\alpha$ -rays were entirely helium.

A paper on "Wave-form Sifters for Alternating Currents" was read by Mr. A. CAMPBELL.

If an alternating current of complex wave form be passed through a condenser (K), and the primary coil of a mutual inductance (M) in series with it, any other circuit connected across the condenser and the secondary coil (in series) will receive no component of the current of frequency  $n$  if  $\omega^2 MK = 1$ , where  $\omega = 2\pi n$ .

This arrangement affords a means of totally suppressing the fundamental or any single harmonic in a complex wave form. This kind of sifting can also be done by means of almost any null method in which the balance depends on frequency. A bridge method suitable for quite low frequencies is also described.

Mr. DUDELL pointed out the value of being able to get rid of particular harmonics, especially of telephonic frequencies. It was very difficult to make a machine to generate a sine wave, and if the wave was not a sine wave the mathematical formulæ did not apply. He thought the chief use of Mr. Campbell's sifter would be to remove the last trace of a troublesome harmonic from a machine that had been designed to give as nearly as possible a pure sine wave. Generally there was only one harmonic that was specially troublesome.

Dr. RUSSELL said that the more usual way of getting current or P.D. waves, which were approximately sine shaped, was to use a resonator, which greatly magnified one harmonic. Prof. G. A. Campbell's "wave-form filter" did this. It consisted merely of a condenser and an inductive coil in parallel. Armagnat's oscillograms proved that excellent results could be obtained in practice by simply tuning a condenser and an inductive coil in series. He deprecated the introduction of too many technical terms into electrical theory.

Prof. G. W. O. HOWE remarked that a disadvantage of the old-fashioned method of getting pure sine waves by resonance was that the amplitude varied so much with slight changes in the frequency of the generator.

The PRESIDENT thought the subject a matter of considerable importance.

The AUTHOR, in reply, stated that his method depended upon the suppression of a troublesome harmonic, and that the result was not much affected by a slight change in frequency. In telephone work it was sometimes very valuable to get rid of the octave of the fundamental. We might obliterate the harmonic at the generator, or just before the current reached the detecting instrument. Iron must not be used in the circuit, or it will reintroduce a suppressed harmonic.

#### Ordinary Meeting, March 22nd, 1912.

Prof. C. H. LEES, F.R.S., Vice-President, in the Chair.

A PAPER ON "A 2000-frequency Alternator" was read by Mr. W. DUDELL.

The author described and exhibited a small 2000-frequency alternator which he had designed and had constructed for testing purposes, mainly in connection with telephonic measurements. The alternator is of the salient pole revolving field type running at 8000 revs. per min. The stator is smooth and would like a gramme ring, the object being to obtain as near as possible a sine wave.

The author gave curves showing the open circuit characteristic, the short-circuit current, and the regulation of the alternator at four different frequencies. The output of the alternator amounted to as much as  $\frac{1}{2}$  kw. at the higher frequencies.

Oscillograph curves of the alternator on open circuit, and when loaded with non-inductive resistance, inductances and condensers were shown. These appeared to be practically sine waves. This is not, however, strictly the case, as there is a slight third harmonic present. To demonstrate this a further set of oscillograph curves of the P.D. of the alternator were exhibited. In taking these curves the non-inductive resistance in series with the oscillograph strips was replaced by a small condenser so as to accentuate the upper harmonics.

The author described an attempt at 2000 frequency, which had failed, to repeat Dr. Thompson's experiment on the effect of an alternating magnetic field on the brain.

Mr. B. S. COHEN stated that Mr. Duddell had supplied one of his alternators to Telephone House, and it had given thorough proof of its reliability and usefulness. He exhibited characteristics and oscillographs taken from the machine. The third harmonic that was present was of no practical detriment. If the capacity of a microfarad mica condenser was found from the current taken by it and the voltage applied, the error was less than 0.5 per cent at a frequency of 1000. The only source of trouble had been in the driving belt, but that had been satisfactorily overcome. The instrument lent itself to a variety of interesting uses. If a telephone be put across the machine when run at the resonating frequency, the amplitude of vibration was such that matches could be blown out at a distance of 3 or 4 metres.

Mr. CHURTON asked whether Mr. Duddell needed a constant voltage at different frequencies, as this would necessitate a very high flux at low frequencies and *vice versa*.

Mr. A. CAMPBELL expressed interest in the efficient manner in which Mr. Duddell had been able to avoid vibration in the mounting of the motor. Even a wire interrupter may disturb a vibration galvanometer (in tune with it) by vibrations mechanically transmitted across a large room. He mentioned that a vibration galvanometer of low ohmic resistance could be used to very largely suppress any harmonic to which the galvanometer was tuned, as the apparent resistance for this harmonic would be very high.

Mr. S. A. POLLOCK described a somewhat similar machine that had been constructed five years ago, and was still running at the G.P.O. The rotor contained 60 poles which were wound zigzag with eight turns of wire. It had been run up to frequencies of 8000, and was perfectly balanced at the highest speed. He exhibited oscillograms of the wave-form. The machine was largely used for measuring the apparent resistance of loading coils. The wave-form was purified by means of sifting circuits. To keep the frequency constant a vibrating reed was placed in series with a split commutator fixed on the shaft of the motor and connected in series with the armature. If the motor ran out of phase with the reed, either an accelerating or retarding current was sent through the armature. A counter and a chronograph always showed that the number of revolutions per minute was exactly the same as the vibrations of the reed.

Dr. W. E. SUMPNER commented on the small drop in voltage at the high frequencies. From a scientific point of view the chief points in the machine were the large air gaps and the unslotted armature. It was to these that the good regulation was due.

The AUTHOR, in reply, stated that the machine supplied to Mr. Cohen was one of the three original ones. In the later ones the armature is wound in three sections, which can all be placed in parallel or in series. This was to avoid having to use a transformer in order to obtain the required voltage which might distort the wave-form. In reply to Mr. Pollock, he stated that the zigzag form of winding was an excellent one for the highest frequencies. He mentioned that Sir D. Solomons had constructed an alternator giving a frequency of 10,000. This was a prototype of the modern alternators giving frequencies of 100,000. In reply to Dr.

Sumpner, he stated that the good regulation possessed by the machine was helpful in avoiding distortion of all kinds. He was indebted to Messrs. Muirhead and Co. for having built the machine.

A paper on "A Method of Comparing the Capacities at Various Frequencies" was read by Mr. A. CAMPBELL.

To compare the capacities of two condensers under conditions similar to those in Maxwell's commutator method, they are charged and short-circuited periodically in two adjacent arms of a bridge by a double rotating commutator, the corresponding contacts being made simultaneously. If the other arms of the bridge are resistances R and S, and a battery and direct-current galvanometer (of long period) are used, then a balance is obtained when  $K_2/K_1 = R/S$ . The method is highly sensitive. Methods (like the above) in which the applied voltage has a square-topped wave-form give results in agreement with those using sine wave-form when the period of charge (and equal discharge) with the square-topped wave is  $2/\pi$  times the half period of the sine wave.

Dr. J. A. FLEMING remarked that Mr. Campbell's suggestion for using a double commutator for comparing capacities in a Wheatstone's bridge is not altogether new. Many years ago a double commutator was made in the Pender electrical laboratory at University College for this identical purpose. Since a condenser plus a commutator behaves like a resistance and lets through a certain quantity of electricity per second, it was an obvious application to insert in the two branches of a Wheatstone bridge two condensers and a double commutator so arranged as to charge and discharge the condensers simultaneously. The method seemed so obvious that he did not trouble to describe it. The double commutator method can also be used with advantage for comparing together by a bridge method, the capacity of a small adjustable air condenser with the capacity of a wireless telegraph antenna. The small air condenser can have its capacity determined by the Carey Foster method, and it is then not necessary to carry about apparatus for standardising the galvanometer.

Dr. RUSSELL queried the utility of finding the ratio of the effective capacities of two condensers having different absorptive properties by a double commutator method. He also asked whether the author's experimental result could not be expressed more simply by saying that the ratio of the effective capacities was the same with sine and square-shaped periodic waves when the charges given to the condensers were the same in the two cases.

Mr. E. H. RAYNER pointed out that in tests of condensers with alternating currents the polarisation was continually reversed, but in the present method the polarisation was always in the same direction.

The AUTHOR, in reply, said that the method does not appear to have been described before. He was interested to hear that Dr. Fleming had been using it for some time past. In reply to Dr. Russell he pointed out that in the alternating-current methods the absorption was separated from the capacity, and hence the latter might reasonably be called the true capacity at the particular frequency used. He did not think Dr. Russell's remark about the curves having equal areas was quite valid. In reply to Mr. Rayner he stated that when, in Maxwell's method, a reversing commutator was used, it gave with a mica condenser exactly the same results as the usual short-circuiting commutator.

A paper on "The Coefficients of Expansion of Fused Silica and Mercury" was read by Mr. H. DONALDSON.

It is shown by experiments on the silica metre of the National Physical Laboratory that the values for the coefficient of expansion of fused silica obtained by previous observers on small specimens by optical methods are confirmed by the comparator method with a long specimen. These values are then used to obtain, from Harlow's ex-

periments (*Proc. Phys. Soc.*, December, 1911, xxiv., 30), values for the mean coefficient of expansion of mercury for the ranges  $0^\circ\text{C. to }100^\circ\text{C.}$ , and  $0^\circ\text{C. to }184^\circ\text{C.}$  The use of these in conjunction with the previous observations of Chappuis on the expansion of mercury leads to the representation of that expansion by the equation:—

$$V_t = V_0(1 + 1.81384 \times 10^{-4}t + 9.862 \times 10^{-8}t^2 + 1.6298 \times 10^{-11}t^3).$$

Other formulæ for the representation of the same quantity are quoted and examined, and it is suggested that further experiments with a silica weight thermometer would go far in elucidating the points of difficulty connected with them.

The hour being late, the discussion on this paper was, on Dr. HARKER's proposal, adjourned till the next meeting.

#### SOCIETY OF CHEMICAL INDUSTRY. (LONDON SECTION).

Ordinary Meeting, April 1st, 1912.

Mr. E. GRANT HOOPER in the Chair.

The following papers were read and discussed:—

"Theory of Sulphuric Acid Manufacture." By W. C. REYNOLDS and W. H. TAYLOR.

The authors show that Raschig's contention that sulphuric acid is formed in the lead chambers by the interaction of nitrous and sulphurous acids, with formation of two hypothetical compounds, nitrososulphonic acid,  $\text{ONSO}_3\text{H}$ , and nitrosulphonic acid,  $\text{H}_2\text{SNO}_5$ , is founded on experimental errors. They have proved (1) that the only gaseous product of the action of sulphurous acid on nitrous acid is nitrous oxide, the nitric oxide formed in Raschig's experiments being due to the presence of potassium iodide as an indicator, (2) that chamber crystals can exist in solution in 60 per cent sulphuric acid, the latter fact invalidating Raschig's account of the formation of Sabatier's violet acid (Raschig's nitrosulphonic acid). Divers' modification of Raschig's theory is also rendered untenable by these facts.

"Estimation of Sulphides in Lime Liquors." By J. R. BLOCKLEY and P. B. MEHD.

The amount of sodium sulphide present in a sulphide-lime liquor is estimated by titration with  $\text{N}/10$  zinc sulphate solution in presence of excess of ammonium chloride. The addition of the ammonium chloride prevents the precipitation of zinc hydroxide, which is obtained if zinc sulphate is added to a lime liquor.

Experiments are recorded of attempts to determine what reactions take place when sodium sulphide and lime are mixed in various ways, and also to determine what are the active compounds for removing the air or wool from hides and skins when such mixtures are used. It is concluded that the active constituent is  $\text{Ca}(\text{SH})(\text{OH})$ , calcium hydroxysulphydrate, in the ordinary commercial mixtures.

The alkalinity of lime liquors is usually taken as a means of judging the age or mellowness, but in presence of sodium sulphide the alkalinity gives no such indication.

Experiments are also recorded on the absorption of sulphides by hides in lime liquors containing sulphides.

Lime liquors and pastes were prepared in the different ways which are used commercially to determine if any difference could be detected in their nature or their action on the hide, but no such difference could be detected.

The amounts of hide substances dissolved by fresh lime solutions, sodium sulphide, and mixtures of lime and sodium sulphide were determined. The amount dissolved by mixtures is much greater than by the separate constituents.



## NOTICES OF BOOKS.

*Fertility and Fertiliser Hints.* By JAMES EDWARD HALLIGAN. Easton, Pa.: The Chemical Publishing Co. London: Williams and Norgate. 1911.

THIS book is an abridgment of a larger work by the same author, entitled "Soil Fertility and Fertilisers." It may be regarded as an introduction to the study of the nature and action of fertilisers, which is sufficiently detailed for the use of the average farmer, or for the student who is beginning a course of agricultural chemistry. The composition of manures, methods of applying them, ways of maintaining the fertility of the soil and getting the greatest possible return from it, are described in simple straightforward language, and the subject is treated from a thoroughly practical point of view. The examples, however, are naturally drawn mainly from American practice, which would restrict the value of the book to English farmers, while a further drawback is the insertion of quite unnecessary and uninteresting illustrations, e.g., that of a hog—not to illustrate its special points, but simply as "one of the sources of bone phosphate."

*Analytical Report, 1911.* Philadelphia: Smith, Kline, and French Company.

THIS analytical report contains the full results of the analysis of the drugs which have been examined by the chemical staff of Messrs. Smith, Kline, and French during the three years from June, 1908 to 1911. In addition a short account is given of the methods adopted in the physiological testing of some drugs, and the titles and brief abstracts of all the papers which have been published by the staff are included.

*La Vie et les Travaux du Prof. Dr. St. de Kostanecki.* ("The Life and Works of Prof. St. de Kostanecki"). By E. NÖLTING.

DR. E. Nörling, the colleague and friend of the late Prof. Stanislas Kostanecki, delivered the lecture which is reproduced in this pamphlet before the Swiss Chemical Society in August, 1911. In the lecture he sketched the life of Dr. Kostanecki, and gave a *résumé* of his chief contributions to chemistry. His career was short but brilliant, and his activity was remarkable. Most of his researches dealt with the synthesis of aromatic derivatives, particularly dyes and colouring matters, and the list of papers he published is an astonishing record; he reached many results of first-rate importance, and by his untimely death organic chemistry has suffered a severe loss.

*Magnetochemie.* ("Magnetochemistry"). By Prof. Dr. E. WEDEKIND. Berlin: Gebrüder Borntraeger. 1911. (3 Mks.).

MAGNETOCHEMISTRY is a growing branch of the science, which has developed particularly rapidly since it has been established that magnetisability is a molecular as well as an atomic property, and also since the diamagnetism of the organic compounds has been made the subject of careful investigation. This monograph treats briefly of the relations between the magnetic properties and the chemical nature of substances; it is written mainly from a chemical point of view, but the author gives an outline of the fundamental principles of magnetism, and describes shortly the methods of research employed. The results which have been obtained in the study of ferromagnetic materials, the magnetism of dissolved salts, the susceptibility of para- and diamagnetic substances are critically discussed and clearly summarised, and a brief account is given of Weiss's magneton theory, which, in the author's opinion, is a most important contribution to chemistry, and will have great influence in the solution of magnetic as well as of purely chemical problems.

*Die Nephritis.* ("Nephritis"). By Dr. MARTIN H. FISCHER. Translated into German by HANS HANDOVSKY and WOLFG. OSTWALD. Dresden: Theodor Steinkopff. 1912. (5 Mks.).

THIS monograph is practically a continuation of one entitled "Das Odem," which the author published a year ago and in which he gave detailed accounts of his experimental work in clinical physiology. This volume contains a full description of the morphological changes occurring in the nerves as a consequence of nephritis, and discusses the treatment of the disease, with some account of typical or specially interesting cases.

*The Value of Quinine in Combating Malarial Fever.* By S. S. ABRAHAMSON. Netherlands: Indies Association for the Promotion of the Interests of the Cinchona Planters. 1911.

THIS small work contains a short popular account of the malarial mosquito and of the febrifuge qualities of quinine. The measures taken by different countries to promote the use of quinine in combating malaria are described, and interesting statistics relating to its consumption are added. The graphical appendix shows in a very striking manner how remarkably the mortality from malarial fever has fallen in Italy since the Government undertook the distribution of quinine.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. cliv., No. 4, January 22, 1912.

**Bromine Compounds of Alkaloids of *Peganum harmala*.**—V. Hasenfratz. —The seeds of *Peganum harmala* contain two alkaloids, harmaline  $C_{13}H_{14}N_2O$ , and harmine  $C_{13}H_{12}N_2O$ . They yield the same dibasic acid, harmic acid, when they are oxidised by chromic acid in presence of acetic acid, and harmic acid is transformed by distillation *in vacuo* into the secondary base, apoharmine. The methyl iodide compound of apoharmine is decomposed by potash yielding methylapoharmine. All four substances readily give monosubstituted bromine derivatives by the action of bromine in acetic solution, and bromine water gives a dibrominated compound with harmine. All these bromine derivatives are monacid bases.

**Action of Caustic Potash on Secondary Alcohols.**—Marcel Guerbet. —When secondary alcohols are heated to about  $230^\circ$  with caustic potash a very small amount is oxidised, giving rise to acids, while the greater part is transformed into condensed alcohols. Thus isopropyl alcohol gives a small quantity of acetic and formic acids, but the chief product is methylisobutylcarbinol formed by the condensation of two molecules of isopropyl alcohol, and 2,4-dimethyl-6-heptanol formed by the condensation of three molecules of isopropyl alcohol. The action of caustic potash on an alcohol of high molecular weight may be employed to determine whether it is a primary or secondary alcohol. If it is the former it is transformed entirely into the potash salt of the corresponding acid, which salt is soluble in water. If it is a secondary alcohol only a very small proportion of acid is formed, and the greater part of the alcohol either remains unchanged or else is transformed into condensed alcohols which float on the surface when the product is taken up with water.

*Berichte der Deutschen Chemischen Gesellschaft,*  
Vol. xlv., No. 2, 1912.

Platinum, Rhodium, and Hydrogen.—A. Sieverts and E. Jurisch.—The authors have determined the solubility of hydrogen at atmospheric pressure in platinum wire from 1340° upwards. It increases as the temperature rises. If platinum saturated with hydrogen is allowed to cool in the gas practically no hydrogen is retained. At room temperature compact platinum takes up no appreciable amount of hydrogen. The power of absorption of platinum for hydrogen is less than that of an equal weight of iron or nickel, and very much less than that of copper. If the temperature is constant the quantities absorbed by platinum wire are proportional to the square root of the pressure of the hydrogen. Carbon monoxide and sulphur dioxide give no indication of solubility in platinum. Precipitated rhodium when heated *in vacuo* gives up considerable amounts of CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub>, and H<sub>2</sub>O. Four grms. of the ignited metal do not dissolve measurable amounts of hydrogen and carbon dioxide between 420° and 1020°.

Magnetisability of Oxides and Sulphides of Vanadium.—E. Wedekind and C. Horst.—The authors have prepared a number of compounds of vanadium, and have calculated their specific susceptibility,  $X$ , from the formula  $X = \frac{K_0}{d} + \frac{F}{F'} \frac{(x' - x_0)}{\rho}$ , where  $F$  and  $F'$  denote the observed pressure, and the pressure on the normal substance  $x'$  and  $x_0$  are the susceptibility of the normal substance and air,  $d$  and  $\rho$  are the true and apparent density of the substance. The results obtained are as follows:—VO,  $X = +50.06 \times 10^{-6}$ ; V<sub>2</sub>O<sub>3</sub>,  $X = +13.88 \times 10^{-6}$ ; VO<sub>2</sub>,  $X = +3.73 \times 10^{-6}$ ; V<sub>2</sub>O<sub>5</sub>,  $X = +0.86 \times 10^{-6}$ ; VS,  $X = +7.22 \times 10^{-6}$ ; V<sub>2</sub>S<sub>3</sub>,  $X = +8.65 \times 10^{-6}$ ; V<sub>2</sub>S<sub>5</sub>,  $X = +12.56 \times 10^{-6}$ ; VN,  $X = +4.13 \times 10^{-6}$ ; VOCl,  $X = +27.16 \times 10^{-6}$ .

New Red Hydrocarbon.—Rudolf Pummerer.—By the distillation of diphenic acid with lime Kerp obtained a red substance, which he described as a pseudo-diphenylketone. The author, however, has found that the substance is a mixture which contains a new hydrocarbon, for which he has suggested the name rubicene. It is a bright red substance of formula C<sub>26</sub>H<sub>14</sub>, and appears to be a condensed di-phenylene-ethene.

*Bulletin de la Société Chimique de France.*  
Vol. xi.—xii., No. 4, 1912.

Solubility of Nickel and Cobalt Perchlorates.—H. Golblum and F. Terlikowski.—The perchlorates of nickel, cobalt, and chromium have very similar crystallographic properties, crystallising in the hexagonal system. Didymium perchlorate crystallises in the cubic system. Nickel and cobalt perchlorates both crystallise with five molecules of water at the ordinary temperature. At -21.3° they contain nine molecules of water of crystallisation. Their solubility is very great, and increases with the temperature. Ni(ClO<sub>4</sub>)<sub>2</sub> is the less stable of the two perchlorates, decomposing at 103° to give a basic salt, and hydrolysing in aqueous solutions. The cryohydratic point of Ni(ClO<sub>4</sub>)<sub>2</sub> is -49°, and that of Co(ClO<sub>4</sub>)<sub>2</sub> is -62.2°.

Utilisation of the Magnetic Field as a Reagent of Constitution.—Paul Pascal.—The unexpected fall of the diamagnetism of monohalogen derivatives is even more marked in the polyhalogen compounds, especially in those in which the atoms of chlorine, bromine, and iodine are attached to the same carbon. Fluorine exhibits some interesting peculiarities. In the dihalogen ethylene derivatives the decrease is approximately that which characterises a double bond, and when the number of halogen atoms is increased the lowering is also accentuated, but not in the same proportion.

Action of Caustic Potash on Primary Alcohols.—Marcel Guerbet.—When heated in sealed tubes to temperatures of 200–230°, the lower members of the series of

primary alcohols give hydrogen and a certain proportion of ethylenic hydrocarbon, while those containing from C<sub>7</sub> upwards are totally transformed into the corresponding acids. Thus with these the caustic potash acts as an oxidising agent,  $C_nH_{2n+1}CH_2OH + KOH = C_nH_{2n+1}CO_2K + 4H$ . With alcohols of lower molecular weight it also acts as a dehydrating agent,  $C_nH_{2n+1}CH_2OH - H_2O + C_nH_{2n} = CH_2$ . With isoamyl alcohol the yield is 91 per cent of the theoretical yield, and alcohols containing more than six atoms of carbon are practically quantitatively transformed into acids.

Development of Active Principles of Medicinal Plants in 1911.—James Burmann.—The author has determined the alkaloids or glucosides in specimens of aconite, belladonna, digitalis, and colchicum grown in the year 1911. On the whole, the year was favourable to the development of toxic principles in these plants. In spite of the dryness of the season the percentages of water showed only very slight variations.

## MISCELLANEOUS.

Faraday Society.—The next meeting of the Faraday Society will take the form of a general discussion on "Magnetic Properties of Alloys." The discussion will take place on Tuesday, April 23rd, at 8 p.m., at the Institution of Electrical Engineers, Victoria Embankment, London, W.C. The meeting will be open to members of the Institution of Electrical Engineers, of the Physical Society of London, and of the Institute of Metals. Others interested in the subject desirous of being present should apply to the Secretary of the Faraday Society, 82, Victoria Street, London, S.W. Sir Robert Hadfield, F.R.S., will preside over the discussion. The following provisional programme has been arranged:—

Prof. E. Wedekind will read a paper on "The Dependence of Magnetisation on Valency in Chemical Compounds."

Dr. Alexander D. Ross and Dr. J. G. Gray will read papers on "The Magnetic Properties of a Variety of Special Steels at Low Temperatures," and on "The Heusler Alloys."

The following papers will be communicated:—

"The Equipment of the Magnetic Laboratory of the Physikalisch-Technische Reichsanstalt, Charlottenburg." By Geheimrat Dr. E. Gümlich.

"The Nature of the Heusler Alloys":—"The Physical Aspect." By Dr. E. Take. "The Chemical Aspect." By Dr. F. Heusler.

"Variation of Ferromagnetic Properties of the Heusler Alloys with Composition and Heat Treatment." By Prof. A. A. Knowlton.

"The Relations between the Mechanical Hardness and the Retentivity and Permeability of Ferro-alloys." By Prof. C. E. Burgess and Mr. James Aston.

The subject will then be open for general discussion.

## MEETINGS FOR THE WEEK.

TUESDAY, 16th.—Royal Institution, 3. "Algernon Charles Swinburne—His Early Life and Work," by Edmund Gosse, LL.D.

WEDNESDAY, 17th.—Microscopical, 8. "Life History of a Marine Diatom from Bournemouth," by J. D. Siddall. "Modified Form of the Lever Fine-adjustment, and a Simple Turnout Device for the Substage Condenser," by E. B. Stringer.

— Royal Society of Arts, 8. "Municipal Chemistry," by J. H. Coste, F.I.C.

THURSDAY, 18th.—Royal Institution, 3. "Synthetic Ammonia and Nitric Acid from the Atmosphere," by Prof. A. W. Crossley, F.R.S.

FRIDAY, 19th.—Royal Institution, 9. "Electricity Supply—Past, Present, and Future," by A. A. Campbell Swinton, M.I.E.E., &c.

SATURDAY, 20th.—Royal Institution, 3. "The Architecture of the Renaissance in France," by Reginald Blomfield.



# THE CHEMICAL NEWS.

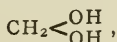
VOL. CV., No. 2734.

## RECENT DEVELOPMENTS IN BAKELITE.\*

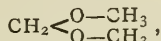
By L. H. BAEKELAND.

My subject involves the use of two main raw materials, phenol or carbolic acid, which is found in gas tar, and formaldehyde. The latter is now manufactured by the oxidation of wood alcohol.

I should state that the name of formaldehyde is used in a rather broad sense. I never have seen real formaldehyde,  $\text{CH}_2\text{O}$ , and very few chemists have had occasion to examine it. It is a gas which can be made to liquefy and solidify by the intense artificial cold attainable by means of liquid air (Raikov, *Chem. Ztg.*, xxvi., 135; xii.; 1901, xi.; Kekulé, *Ber.*, xxv., 2435; Harries, *Ber.*, xxxiv., 635). Solidified  $\text{CH}_2\text{O}$  melts at  $-92^\circ\text{C}$ . The commercial product, designated ordinarily under the name of formaldehyde, is a watery solution of formaldehyde, containing at the same time variable proportions of methyl-alcohol. In these solutions formaldehyde is present partially as methyleneglycol—

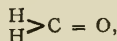


and as methylal—

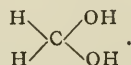


accompanied with variable amounts of several distinct polymers of formaldehyde, of polymers of methyleneglycol, or polymers of partial anhydrides of methyleneglycol, more or less directly related to paraform, trioxymethylene, and similar substances.

The thermochemical researches of Delepine had already shown (*Comptes Rendus*, cxxiv., 1454; *Bull. Soc. Chim.*, xvii., 849), in watery solutions, the existence of stable hydrates, which are not decomposed by distillation, and the later work of Auerbach (F. Auerbach, also Auerbach and Barschall, *Arb. Kais. Gesundh.*, Band xxii., Heft 3 and Band xxvii., Heft 1, Verlag Julius Springer, Berlin), leave no further doubt on the very complicated composition of so-called formaldehyde solutions. The latter are merely mixtures of various chemical compounds which ultimately react in the same way as  $\text{CH}_2\text{O}$ , and which, for practical purposes, are equivalents for each other in the chemical reactions where formaldehyde or methylene-compounds are used. The main point in all these reactions is that the group methylene =  $\text{CH}_2$  should exist in a mobile condition. It matters little whether this group =  $\text{CH}_2$  presents itself as true formaldehyde or oxymethylene—



or as its hydrate as methyleneglycol,

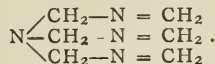


The same remark applies to its polymers, paraform, trioxymethylene, or other polymers of formaldehyde, or polymers of methyleneglycol, or partial anhydrides thereof. All these substances can be substituted for each other, and the final result of the reaction can be made practically the same.

So well was this known that the early work of Ad. Baeyer and his pupils on condensation products of phenols

and formaldehyde was carried out by means of the latter's methylene representatives—methylal, methyleneacetate, methylenechloride, or methyleneiodide—for the simple reason that commercial formaldehyde, was unavailable at that time.

Ammonia combines very easily with formaldehyde, and forms hexamethylenetetramine (see Wohl, *Ber.*, xix., 1892; Tollens, *Ber.*, xvii., 653; "Carl Goldschmidt," p. 29; Verlag von Friedrich Cohn, Bonn, 1903)—



So eager is the tendency of combining with ammonia, that if formaldehyde, or any of its equivalent compounds, which keep the group  $\text{CH}_2$  in mobile condition, is put in presence of an ammonium salt, like ammonium chloride, acid is expelled, and hexamethylenetetramine is formed (see Cambier, Brochet, *Comptes Rendus*, cxx., 557).

Consequently, whenever an excess of formaldehyde or a formaldehyde compound is put in presence of ammonia or an ammonium salt, hexamethylenetetramine is formed forthwith, so that mixtures of ammonia and formaldehyde, or hexamethylenetetramine, are practically the same thing. On the other hand, hexamethylenetetramine, in presence of acids, re-liberates easily formaldehyde. There is nothing astonishing that in the condensation of phenols and formaldehyde we should be able to replace formaldehyde by other related compounds.

Let it then be understood that in the reaction I am about to explain, whenever I refer to formaldehyde, this broad denomination includes many substances which are practically equivalent in their chemical action to the orthodox but elusive true formaldehyde,  $\text{CH}_2\text{O}$ .

When phenol is acted upon by means of formaldehyde, or its equivalents, a most varied set of reactions can occur; even by starting from the same raw materials new substances may be produced which, according to conditions of operation, may vary considerably in appearance, as well as in chemical and physical properties.

The earlier investigators, like Ad. Baeyer and others (*Ber.*, v., 1095; xix., 3004, 3009; xxv., 3477; xxvii., 2411), were especially on the look-out for substances of definite chemical constitution, which could be easily isolated, crystallised, and purified for the development of their purely scientific work; if they obtained non-crystalline bodies, of resinous appearance, this was merely considered as a drawback, and constituted an unpleasant obstacle in their theoretical research work. Their resins did not seem to attract much of their attention, and the study of the resinous products was soon abandoned in favour of the crystalline bodies which could be obtained. Under the circumstances it is quite natural that no special effort had been made to produce these resinous bodies under such conditions that they could be used for definite technical purposes.

When in 1891 formaldehyde had become a relatively inexpensive article of commerce, Kleeberg (*Ann.*, cclxiii., 283) took up this matter anew, and found that by bringing together a mixture of formaldehyde solution, phenol, and hydrochloric acid, a violent reaction ensues, and the whole mass changes to an amorphous hard resinous body, of irregular shape, a mixture of various heterogeneous substances, including remnants of the reacting materials. He was confronted by the fact that trying to purify this substance, or to establish a constant composition, was a rather thankless job, especially so as the biggest part is insoluble and not amenable to the usual methods of purification; after giving a limited attention to this subject, he pursued his work along the line of other condensation products which can be obtained in crystalline form.

Afterwards various attempts were made by Smith, Luft, Blumer, Story, DeLaire, and others to try to modify this reaction so as to produce more definite bodies than those obtained by Kleeberg (see Baekeland, *Journ. Ind. and Eng. Chem.*, i., No. 3, March, 1909). Their efforts were

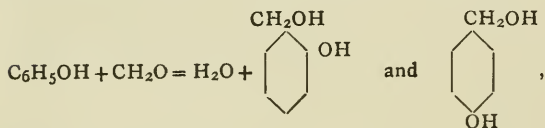
\* Read at joint meeting of New England Section, Am. Chem. Soc. and Soc. Chem. Industry, Boston, November 10, 1911. From the *Journal of Industrial and Engineering Chemistry*, iii., No. 12.

directed towards moderating the reaction by limiting the temperatures, or by diluting the reacting materials in suitable solvents. It was thus found that, according to circumstances, resins could be obtained which are soluble in alcohol and similar solvents, and which can be heated and melted, and which under treatment of heat remain indefinitely fusible, and behave much like shellac or similar natural resins. For that reason they are called shellac-substitutes, and I have published a special paper on this subject (see Baekeland, *Journ. Ind. and Eng. Chem.*, i., No. 8, August, 1909), in which I designate these artificial soluble and fusible resins under the general name of Novolak.

Under other conditions entirely different bodies are obtained, which, although resinous in appearance, can no longer be considered as true resins, and lack the chemical characteristics of resins. They are infusible and insoluble. However, the preparation of these infusible substances involved several objectionable conditions, which made them of little, if any, practical value. All this is described in my former publications on this subject (see Baekeland, *Ibid.*, i., No. 3, March, 1909; i., No. 8, August, 1909).

I undertook a systematic study to establish the chemical constitution and the relation which exists between these infusible bodies, the fusible, soluble, resinous condensation products, and the substances from which they are derived. I was able to dissect this perplexing reaction in several distinct transition stages, which can be produced at will. It seemed at first that the formation of these very dissembling bodies was simply a matter of relative proportions of reacting materials, or of quantity of condensing agents, but I became convinced that this is not so simple and that the reaction involved several, until then unobserved or neglected, phenomena which have a paramount bearing on the results.

By conducting the process in several stages, and more particularly by effecting the synthesis from different starting points, I succeeded in gaining enough insight into the problem that I could devise some sure practical methods for obtaining new results. Since then several years of uninterrupted hard work have enabled me to devise various technical applications, with most of which you are already acquainted. One of my first problems was to determine why different experimenters had obtained such dissimilar results when starting from almost identical products. For instance, Lederer (*Journ. Prakt. Chem.*, [2], i., 224) and Manasse (*Ber.*, 1984, 2409—11; D. R. P., Baeyer, 85,588; U.S. P., Manasse, 525,786, 1894) by acting with 1 molecule of  $\text{CH}_2\text{O}$  on 1 molecule of  $\text{C}_6\text{H}_5\text{OH}$ , in presence of 1 molecule of  $\text{NaOH}$ , then acidulating, obtained ortho- and paraoxybenzylalcohol,



which is a nicely crystalline water-soluble body, known also as saligenin, very different from the resinous amorphous condensation products. Saligenin had formerly been prepared from its glucoside, salicine, which was extracted from the willow tree.

Then again, De Laire (French Patent, No. 361,539), operating under rather similar conditions, using about the same proportions of alkali, phenol, and formaldehyde, then acidulating, and heating afterwards, obtained fusible soluble resins of totally different character than oxybenzylalcohol. These resins are identical with the soluble fusible resins which he and others obtained by heating directly acids with a mixture of formaldehyde and phenols, but they are totally different from the infusible insoluble mass Kleeberg and others obtained by heating hydrochloric acid with the same mixture of phenol and formaldehyde. At that time those results seemed rather irreconcilable with each other,

and it very often happened that two operators, starting from the same mixtures, obtained totally different products by simply changing somewhat their way of working. Some workers in this line seemed to pin their faith to the fusible soluble resins, or Novolak, and used every means to exclude the disturbing insoluble bodies which tended to form. Others again, tried to utilise the infusible bodies. It soon became evident to me that the bodies of the latter kind prepared up till then had not attained their full best qualities, because they were produced at too low a temperature in presence of acids and in admixture with solvents or with an excess of phenol.

I found that decidedly higher temperatures than those preconised for these products were very desirable, not only for improving the end product but more especially for insuring rapid formation and rapid moulding. But when I tried to employ high temperatures I was immediately confronted, like my predecessors, with the same difficulties, namely, high temperatures bring about violent uncontrollable reactions, accompanied with self-heating and with the evolution of gaseous products, which render the mass porous. This was the very reason why those who had preceded me had carefully recommended in all their descriptions not to use temperatures exceeding  $50^\circ$  to  $80^\circ \text{C.}$ , or at the utmost  $100^\circ \text{C.}$ ; even then they were compelled to use solvents, or, in some cases, an excess of phenolic body so as to moderate the reaction by these diluents.

I became aware of the fact that the disturbing emission of gaseous products, whenever the reaction is carried out at too high a temperature, has the characteristics of chemical dissociation. Its disturbing action could be moderated by introducing a solvent, for instance, an excess of phenol, in which the gaseous products could provisionally accumulate until they established a dissociation equilibrium. But I concluded that the easiest and most practical way to prevent gaseous dissociation, and the resulting porosity of the mass, was to exert a suitable counter-pressure. This allows us to use as high a temperature as we may desire, by increasing the counter-pressure accordingly. This can be done in several ways, either by heating in a closed vessel in which the pressure raises by itself, or better in a vessel in which air or another gas is pumped, under pressure, before the heating begins. One of the most practical ways, and specially suitable for moulding, is the use of a heated hydraulic press.

Permit me to say here that before I took up this subject, no other methods for moulding infusible condensation products of phenols and formaldehyde had been suggested than so-called cast-moulding, consisting in pouring the original mass in a mould and heating moderately without pressure until solidification sets in.

The technical problem was advanced further by utilising the following observation:—

If formaldehyde and phenols are heated in presence of an acid condensing agent, an insoluble body may or may not be the result. This does not depend on the amount of acid nor whether the reaction is allowed to proceed violently or slowly; neither does it depend on the amount of formaldehyde which has been used; but it all depends on the amount of formaldehyde which has really entered into reaction. For instance, if the reaction be carried out in presence of an acid condensing agent, with an amount of phenol exceeding 15 molecules of phenol for 14 molecules of formaldehyde, a fusible soluble resin of the Novolak type is most likely to form. The same thing occurs even if large amounts of formaldehyde are used, but if for some reason or another enough formaldehyde is volatilised or otherwise lost during the reaction.

I found that these uncertainties do not exist if, instead of an acid condensing agent, we use a small amount of a base. Bases had been used before but in much larger proportions, by which they form substances entirely different from those I have in view. Relatively small amounts of ammonia, alkalis, amines, or other basic substances, added



to a mixture of phenols and formaldehyde, enabled me in every case, after heating, to produce insoluble infusible end-products, regardless whether the amount of phenol is or is not in excess. With the use of small amounts of basic condensing agents there is no longer any doubt as to the result, and the reaction becomes so easy to control as to lend itself to the most varied industrial applications. By the use of bases the initial reaction can easily be interrupted at will, so as to obtain stable intermediate products, which simplify the whole process so as to make it a practical industrial operation. Furthermore, the presence of these small quantities of bases in the initial condensation product accelerates, at relatively low temperatures, the final hardening by polymerisation. This beneficial accelerating action is so pronounced that, with some precautions, the process of hardening can be carried out in a much shorter time, and without the use of any counter-pressure; for instance, by starting at relatively moderate temperatures, say, about 80° C., and as soon as the mass begins to harden by raising the temperature with increasing rapidity to 110° C. and over. For very thin layers this precaution of gradual heating can even be omitted, and the maximum temperature can be applied at once, without any danger of blisters or porosity.

However, in most cases it is decidedly more practical to heat directly at maximum temperature, under suitably increased pressure. In this way hardening and moulding can be accomplished in as short a time as one to five minutes, according to the thickness or the size of the object. My published patents contain a description of these processes, and I shall limit myself to the following brief description.

About molecular proportions of phenol and formaldehyde are boiled in presence of suitable amounts of ammonia or sodium hydroxide. This gives an initial product which is called A, and which can be purchased in the trade either in liquid or in solid condition. A is the immediate and first result of the condensation reaction, whereby formaldehyde in reacting upon phenol increases the carbon nucleus of its molecule, this phenomenon being accompanied by a corresponding chemical elimination of water. This A, our initial condensation product, is soluble in alcohol, acetone, and similar solvents. Certain varieties of A can be kept indefinitely, or at least for a long time, without alteration. A is characterised by the very distinct property that when it is further heated it will ultimately be transformed into a final infusible insoluble substance, of great hardness, called Bakelite "C," and this is the final product at which we aim in the whole process.

Solid A, on account of its physical appearance and its solubility in alcohol or acetone, might easily be mistaken for one of the permanently fusible soluble resins of the Novolak type. But such a mistake is impossible if we bear in mind that Solid A, when heated, although it may melt for awhile, soon becomes hard, infusible, and insoluble by polymerisation. Novolak, on the contrary, if heated, simply melts and sets again by cooling, but it does not harden to an infusible insoluble body by simple application of heat.

(To be continued).

Sixth Congress of the International Association for Testing Materials.—The Sixth Congress of the International Testing Association, under the patronage of the President of the United States, will be held at New York, in the Engineering Societies' Building, from Tuesday, Sept. 3rd, to Saturday, Sept. 7th, 1912. The President of the Congress will be Prof. H. M. Howe, of Columbia University. A large number of papers will be read and discussed, and arrangements are being made for visits and excursions to other cities in the United States. Members of the Iron and Steel Institute desirous of participating in the Congress can obtain further information on application to G. C. Lloyd, Secretary of the Institute.

# THE 'PHENOMENON OF OCCLUSION IN PRECIPITATES OF BARIUM SULPHATE, AND ITS RELATION TO THE EXACT DETERMINATION OF SULPHATE.\*

By JOHN JOHNSTON and L. H. ADAMS.

(Concluded from p. 175).

## (b) Precipitation by means of an Acid Solution of Barium Chloride.

FOR these experiments we made up a solution containing 23 grms. BaCl<sub>2</sub>·2H<sub>2</sub>O in a litre of 10 per cent HCl (this corresponds nearly to saturation); 90 cc. of this solution are required for the precipitation of 2 grms. of barium sulphate. In the precipitation, 100 cc. were run slowly (in about ten minutes) into the boiling and constantly stirred solution of the sulphate. The remaining manipulation was exactly as in (a); but the occlusion was not determined. The results follow.

Original solution contained—

| NaCl. | 40 per cent HCl. | BaSO <sub>4</sub><br>calc. | BaSO <sub>4</sub><br>found. | Deficit<br>(uncor.). |
|-------|------------------|----------------------------|-----------------------------|----------------------|
| Grms. | Cc.              | Grms.                      | Grms.                       | Mgrms.               |
| 0     | 0                | 1·9923                     | 1·9878                      | 4·5                  |
| 5     | 0                | 2·0183                     | 2·0017                      | 16·6                 |
| 0     | 25               | 1·9894                     | 1·9884                      | 1·0                  |
| 5     | 25               | 2·0039                     | 1·9980                      | 5·9                  |

In this method of precipitation, the concentration of the barium chloride is much smaller (2 per cent as against 10 per cent), and consequently the amount of chloride occluded is smaller; furthermore, the bulk of the precipitate is formed in a less strongly acid solution than in (a), and therefore the occlusion of sulphate is greater. These two influences together make the deficits larger than in (a). Consequently this method is not so good as the former, in which all the acid was present in the original solution; it is besides less convenient.

## (c) Precipitation in Neutral Solution and Subsequent Digestion of the Precipitate with Concentrated Hydrochloric Acid.

In these experiments the precipitation was made slowly in neutral solution; immediately thereafter, the whole was evaporated to dryness, and then digested with occasional stirring, for twenty-four hours at 100° with 50 cc. 40 per cent HCl. It was then evaporated to dryness, taken up with water, filtered, and washed as usual. The ignited precipitates were very hard and flinty, thus indicating considerable contamination; this was confirmed on determining the amount of sulphate occluded. The results, after applying the correction for occlusion of sulphate (on the assumption in this case that it was entirely Na<sub>2</sub>SO<sub>4</sub>), are considerably too high, and indicate the occlusion of considerable chloride in addition to the sulphate, the presence of which was shown directly.

|                                               |                |        |        |
|-----------------------------------------------|----------------|--------|--------|
| Original solution contained                   | NaCl (grms.)   | 0      | 5      |
|                                               | HCl (cc.)      | 0      | 0      |
| BaSO <sub>4</sub> calculated (grms.)          | .. .. .        | 2·0020 | 2·0076 |
| BaSO <sub>4</sub> found (grms.)               | .. .. .        | 2·0023 | 2·0040 |
| Deficit, uncorrected (mgrms.)                 | .. .. .        | -0·3   | 3·6    |
| Occlusion (mgrms.)                            | Found          | 6·4    | 12·5   |
|                                               | Correction (a) | 4·5    | 8·7    |
| Error (a), corrected for occlusion (per cent) |                | 0·24   | 0·26   |

(a) On the assumption that the occluded sulphate is wholly Na<sub>2</sub>SO<sub>4</sub>.

Here, therefore, although the agreement between the amounts of barium sulphate found and calculated is fairly good, it depends upon a compensation of large errors, conditioned by the fineness of the precipitate. Barium sulphate precipitated from neutral solution is extremely

fine-grained; the contamination is not removed with sufficient completeness even by digestion for twenty-four hours with hot concentrated hydrochloric acid. This method is also burdened with the added difficulty of manipulating the very fine-grained precipitates, which exhibit a marked tendency to adhere to all surfaces with which they come in contact.

#### *General Conclusions on the Exact Determination of Sulphate.*

The method given by Allen and Johnston gives correct results, but has the disadvantage for general analytical work that one must apply three corrections, two of which are somewhat troublesome to determine. This inconvenience is, in part, obviated by the fact that the corrections are constant for any particular set of conditions, and so need only be determined once for all. A better plan would probably be to calibrate the method by sulphate determinations on *pure dry* sodium (or potassium) sulphate dissolved in a medium as similar as possible to that in which the sulphate to be analysed is dissolved. Sodium (or potassium) sulphate is easily obtained in a pure dry state (by re-crystallising, if necessary, and heating to 200° in an air-bath for an hour; its purity may be easily controlled by an accurate determination of its sulphate content); so that the errors inherent in such a method of calibration should be very slight, if the conditions of precipitation were reproduced at all closely.

The foregoing experiments show that none of the methods tried is suitable for accurate work because their apparent correctness depends upon a compensation of errors. In the precipitations in strongly acid solutions, however, these errors are all small, and the results are consequently reproducible with considerable accuracy; this method might then well be calibrated in the way suggested above. It possesses the advantage, as compared with the method of the previous paper, that it is easier to manipulate and much more rapid; for one may evaporate to dryness *immediately* after precipitation, and the precipitate, being coarse-grained, does not adhere at all to the vessel, is quickly filtered and easily washed, and with less danger of loss in any of the operations. By making concurrent comparison determinations it should be possible in the course of a few hours to determine sulphate with an accuracy of  $\pm 0.05$  per cent in any solution the composition of which is known approximately—a condition which very frequently obtains in practice. (If the composition of the solution is not known, recourse must be had to the method in which all of the corrections are actually determined). It would, of course, be preferable always to have the original solution free from the heavy metals and nitrates, as is usually the case in making sulphate determinations.

In conclusion, we may express our belief that there is little chance of discovering any exact method which shall at the same time be generally applicable and require no corrections, and yet not owe its accuracy to a compensation of errors; for the reason that some of the requisite conditions appear to be mutually incompatible.

#### *Summary.*

The occlusion by barium sulphate of other sulphates is a general phenomenon. The amount of this occlusion depends upon (a) the composition of the original solution, (b) the fineness of the precipitate, which in turn is conditioned by the degree of solubility of barium sulphate in the particular medium, the rate of precipitation, and the time and manner of standing between precipitation and filtration. The phenomenon is therefore in all probability an absorption at the surface of the grains of the precipitate, since it is affected by the factors just mentioned.

On the basis of the knowledge gained in this way, attempts were made to find a direct method for the determination of sulphate which should be generally applicable, exact, and require only small and easily determined corrections. We suggest the following procedure: To the solution

(300 cc. for a precipitate to weigh 2 grms.) add 50 cc. of concentrated hydrochloric acid, heat to boiling, and precipitate, stirring constantly, with a 10 per cent solution of barium chloride. This should be added at such a rate that about four minutes is required in running in the 22 cc. necessary; the rate is best regulated by attaching a suitable capillary tip to the burette containing the barium chloride solution. Evaporate the whole to dryness on the steam-bath (this may be done immediately after precipitation), take up with hot water, filter through paper, wash until the washings are free from chloride, ignite very carefully (so as to obviate reduction), and heat to constant weight over a Bunsen burner. The necessary correction is determined by a concurrent calibration of the method; that is, by dissolving an equivalent weighed amount of pure dry sodium (or potassium) sulphate in a medium such that the resulting solution is as nearly as may be of the same composition as the solution to be analysed; the sulphate in this comparison solution is then determined precisely as above. The difference between the calculated amount of barium sulphate and that actually found is the correction to be applied to the weight of the precipitate obtained in the actual analysis.

This procedure, as compared with that advocated by Allen and Johnston, is easier and much more rapid; it is, however, not so generally applicable, but may be used whenever the composition of the solution containing the sulphate to be determined is known approximately; and, we believe, will yield results, accurate to  $\pm 0.05$  per cent of the total sulphate present, in most cases likely to occur in general analytical work.

## THE DETERMINATION OF COPPER.

### A MODIFICATION OF THE IODIDE METHOD.

By E. C. KENDALL.

For the determination of copper the most important methods are the electrolytic, the iodide, and the cyanide. As the determination by means of the electrolytic method requires a considerable amount of time and apparatus, the only methods for the rapid estimation of copper are the iodide and the cyanide.

Upon an examination of the two volumetric methods mentioned, it is apparent that in respect to the amount of time and attention required for a determination the cyanide has a great advantage over the iodide method. However, in respect to the accuracy of the results obtained the iodide method is conceded to be by far the more accurate of the two. As every consideration would be in favour of the iodide method if it could be modified in such a way as to make it as rapid and easy of manipulation as the cyanide method, an attempt was made to make such a modification.

In the determination of copper by the iodide method the copper may be originally present as copper, copper oxide, or sulphide. The first step is to obtain the copper in solution. Practically the only way to do this is to dissolve it in nitric acid. The solution of the copper with nitric acid produces nitrous acid in the solution, and it is the removal of this which causes the delay in the estimation of the copper. As the method is described in the literature, the nitrous acid is destroyed with bromine, the excess of bromine being removed by boiling, or the nitrous acid is removed by evaporating to dryness.

The modification of the iodide method as described in this paper consists in the destruction of the nitrous acid without boiling. This is accomplished by the addition of a small amount of sodium hypochlorite. The addition of sodium hypochlorite to a nitric acid solution produces hypochlorous acid. The interaction of hypochlorous acid and nitrous acid results in the oxidation of the nitrous acid and the formation of hydrochloric acid, and the reaction between hypochlorous and hydrochloric acid results in the



destruction of the hypochlorous acid and the formation of free chlorine and water. As the solution of sodium hypochlorite contains small amounts of chlorides, hydrochloric acid will always be present when the solution is acidified, thus insuring the destruction of the hypochlorous acid and the formation of free chlorine. We thus see that the effect of adding sodium hypochlorite to the solution is the complete destruction of the nitrous acid and the formation of free chlorine.

To remove the free chlorine in solution some compound must be added which will take up the chlorine, but will not affect subsequent operations. Such a compound is found in phenol. Under the conditions of the determination, phenol will add chlorine directly to the benzene ring, but is not affected by iodine or any of the other compounds in the solution. Chlorophenol not being ionised removes all traces of free chlorine.

This modification of the method greatly reduces the time and attention required for a determination, and, in addition, the copper solution is prepared in such a way that iodine can be liberated by copper alone.

In the determination, the copper, copper oxide, or sulphide is dissolved in nitric acid. After the addition of the sodium hypochlorite and phenol, which requires but a moment, the solution is made slightly alkaline with sodium hydroxide, and is then made acid with acetic acid, when the solution is ready for titration. Potassium iodide and starch are added, and the titration is made to the disappearance of the starch iodide colour. There is never any fear of the blue colour "flashing back," and the solutions will remain colourless indefinitely after the titration. As the ionisation constant for acetic acid is too low to allow nitrates to liberate iodine, the amount of nitric acid in solution is immaterial. Even 20 cc. of concentrated nitric acid will not affect the titration. However, too great an acidity is to be avoided, as nitrophenol will be formed. The presence of nitrophenol prevents the determination of copper, but there is no danger of its formation even in the presence of a large amount of acid if the solution is neutralised soon after the addition of the phenol. If a large amount of nitric acid is used to dissolve the copper, it should therefore be partly neutralised before addition of the phenol.

As chlorine easily oxidises phenol to compounds which prevent the determination of copper, it is essential that all of the phenol be added quickly to the solution. Under these conditions the chlorine adds directly to the benzene ring, but if the phenol is added drop by drop the chlorine will oxidise it, producing coloured compounds in solution.

In order to add the phenol quickly enough to the solution it may be poured in from a beaker, or, a more convenient way, from a pipette from which the tip has been removed so that the delivery is from an opening which is of the same bore as the rest of the tube. By forcing the phenol out of such a pipette with the breath the entire volume is added very quickly, and at the same time the phenol is well mixed with the contents of the flask.

After addition of the phenol the chlorine gas which is in the flask above the liquid is removed by blowing it out with the breath, and the sides of the flask are washed with a jet of water from a wash bottle. There should be no odour of chlorine just before the solution is made alkaline.

It should be remembered that the end-point of the titration is not pure white. Cuprous iodide has a cream colour, and when a large amount of copper is present the cuprous iodide gives a decided tint to the solution. When the end-point is nearly reached a drop of the thiosulphate is allowed to fall into the centre of the flask. If a change of colour occurs the solution is given a slight rotary motion, and after the solution is again quiet another drop of the thiosulphate is added. This "spot test" is easily recognised, and gives a very accurate end-point.

The speed of reaction of the copper with potassium iodide varies with the volume. In a small volume the action is rapid, and all of the iodine is liberated at once, but in a large volume an appreciable time may be required

for all of the copper to react. This is especially noticeable when a small amount of copper is present. A high concentration of potassium iodide greatly assists the liberation of the iodine. Accurate results can not be obtained unless at least 3 grms. of potassium iodide are added, irrespective of the amount of copper present, up to 500 mg. of copper.

The solutions required are:—

A. *The Sodium Hypochlorite* solution is made by boiling together a mixture of 112 grms. of calcium hypochlorite and 100 grms. of anhydrous sodium carbonate in 1200 cc. of water. After the calcium is precipitated as carbonate, the solution is filtered and its strength found as follows: 5 cc. of the hypochlorite solution are added to 100 cc. of water containing 5 cc. of 30 per cent potassium iodide solution, and a few cc. of dilute hydrochloric acid are added. The liberated iodine is titrated with 0.1 N sodium thiosulphate. The volume of the solution is now adjusted so that 5 cc. of the hypochlorite solution are equivalent to 30 cc. of 0.1 N sodium thiosulphate.

B. *Phenol*.—A 5 per cent colourless solution of phenol.

C. *Sodium Hydroxide*.—A 20 per cent solution.

D. *Acetic Acid*, 50 per cent.

E. *Potassium Iodide*.—A convenient way to use this is to prepare a solution which contains 30 grms. per 100 cc. of solution. Then 10 cc. will contain 3 grms., which is the amount needed for a determination.

F. *Sodium Thiosulphate*.—For the accurate titration of the liberated iodine two solutions are used. One strong solution, 1 cc. of which equals 6 mg. of copper, and a weak solution, 1 cc. of which equals 1 mg. of copper. The strong solution is run in until the iodine liberated by the copper gives a light straw colour to the solution. Starch is then added, and the titration is finished with the weak solution.

(The weights given here are for calcium hypochlorite, having 35 per cent or more available chlorine).

As a thiosulphate solution loses strength it should be re-standardised from time to time. A convenient way to do this is as follows:—A solution of sodium thiosulphate, approximately 0.1 N, is made by dissolving 24 grms. of the crystallised salt per litre of water. After the solution has stood at least twenty-four hours it is standardised against copper by the method described below. Pure electrolytic copper which has been cleaned with emery paper should be used. After dissolving 150 to 200 mg. of the copper in 6 to 8 cc. of 50 per cent nitric acid the solution is treated as described below, and the thiosulphate is then standardised with this known weight of copper. The most convenient means of re-standardising the thiosulphate is to use a solution of acid potassium iodate. Acid potassium iodate has the formula  $\text{KIO}_3 \cdot \text{HIO}_3$ , so that a normal solution has one-twelfth the molecular weight in grms. per litre. A 0.1 N solution is prepared by dissolving 3.249 grms. of the salt in 1 litre of water, and it is standardised against a known strength of thiosulphate as follows:—Add 10 cc. of the acid iodate solution to 150 cc. of water containing 0.5 to 1 cc. of hydrochloric acid. Upon the addition of potassium iodide, iodine will be liberated according to the equation  $\text{HIO}_3 + 5\text{HI} = 3\text{H}_2\text{O} + 6\text{I}$ . Starch is added and the titration is made to a colourless solution. From this titration the weight of copper, to which 20 cc. of this solution are equivalent, is accurately determined. A 20 cc. pipette is passed through a one-hole stopper, and is allowed to remain in the acid iodate bottle. The end of the pipette is closed with a small rubber stopper. The exact copper equivalent of a thiosulphate solution is now easily found by titrating 20 cc. of the acid iodate solution whose copper equivalent is known with the thiosulphate as described above. The acid iodate remains constant indefinitely.

G. *Starch for Indicator*.—The best preparation for this purpose is a 0.5 per cent solution of Kahlbaum's soluble starch. This is prepared as ordinary starch, but gives a perfectly clear solution which is very sensitive with iodine. If ordinary starch must be used it should be free from all cloudiness.

*Detailed Description of the Method.*

If the copper to be determined is present as metallic copper, 200 to 300 mg. are placed in a 300 cc. flask and dissolved in 5 to 10 cc. of 50 per cent nitric acid.

If the copper is present as cuprous oxide it is filtered on a Gooch crucible through asbestos. The cuprous oxide is then dissolved through the Gooch crucible with 10 to 15 cc. of 30 per cent nitric acid into a 300 cc. Erlenmeyer flask.

If the copper is in the form of sulphide, it is filtered on a Gooch crucible which has a layer of asbestos one-eighth inch in thickness. The crucible is then placed in a small beaker of 50 cc. capacity, and 10 cc. of 50 per cent nitric acid are added. The beaker is placed on a hot plate, and the nitric acid allowed to boil until all the black sulphide has gone into solution. The crucible is then washed off, and the solution transferred to a 300 cc. Erlenmeyer flask. The presence of the asbestos in the solution does not interfere with the titration of the copper.

If the copper to be determined is already in solution as sulphate, chloride, or other salt, sufficient solution is taken to give 100 to 300 mg. of copper.

Having obtained the copper in solution, preferably in a 300 cc. Erlenmeyer flask, the volume being between 50 and 60 cc., the acidity is adjusted to equal 4 to 5 cc. of concentrated nitric acid. A greater volume of acidity is to be avoided. The temperature should not be above 25°. Five cc. of the hypochlorite solution are now added to the copper solution, which is well mixed with a rotary motion. As soon as the colour of the copper solution changes from a clear blue to a greenish tint sufficient hypochlorite has been added. Another indication of a sufficient amount of hypochlorite is the liberation of chlorine. For weights of copper up to 200 mg., 2 to 3 cc. of the hypochlorite are sufficient.

*Determination of Copper.*

| Copper taken.<br>Mg. | Copper found.<br>Mg. | Error.<br>Mg. | Error.<br>Per cent. |
|----------------------|----------------------|---------------|---------------------|
| 20'00                | 20'01                | +0'01         | +0'05               |
| 20'00                | 19'99                | -0'01         | -0'05               |
| 20'00                | 20'00                | -0'00         | 0'00                |
| 30'00                | 29'99                | -0'01         | -0'03               |
| 30'00                | 30'00                | -0'00         | 0'00                |
| 40'00                | 39'98                | -0'02         | -0'05               |
| 40'00                | 39'96                | -0'04         | -0'10               |
| 60'00                | 60'01                | +0'01         | +0'02               |
| 60'00                | 60'01                | +0'01         | +0'02               |
| 80'00                | 80'12                | +0'12         | +0'15               |
| 80'00                | 80'03                | +0'03         | +0'04               |
| 80'00                | 79'98                | -0'02         | -0'02               |
| 80'00                | 79'98                | -0'02         | -0'02               |
| 100'00               | 100'00               | 0'00          | 0'00                |
| 100'00               | 99'99                | -0'01         | -0'01               |
| 120'00               | 119'95               | -0'05         | -0'04               |
| 140'00               | 140'00               | 0'00          | 0'00                |
| 60'00                | 160'00               | 0'00          | 0'00                |
| 160'00               | 160'00               | 0'00          | 0'00                |
| 180'00               | 180'00               | 0'00          | 0'00                |
| 180'00               | 180'00               | 0'00          | 0'00                |
| 200'00               | 200'00               | 0'00          | 0'00                |
| 200'00               | 199'9                | -0'01         | -0'05               |
| 203'2                | 203'2                | 0'00          | 0'00                |
| 220'2                | 220'1                | -0'01         | -0'05               |
| 240'0                | 240'0                | 0'00          | 0'00                |
| 240'0                | 240'2                | +0'2          | +0'08               |
| 261'6                | 261'6                | 0'00          | 0'00                |
| 280'0                | 280'0                | 0'00          | 0'00                |
| 280'0                | 280'3                | +0'3          | +0'10               |
| 300'0                | 300'1                | +0'1          | +0'03               |
| 320'0                | 319'9                | -0'1          | -0'03               |
| 320'0                | 319'9                | -0'1          | -0'03               |
| 340'0                | 340'0                | 0'00          | 0'00                |

NOTE.—The sum of the + and - errors very nearly equals zero.

For larger amounts of copper more hypochlorite may be needed, but 5 cc. will be sufficient for any amount of copper which would be determined by this method. The reactions between the hypochlorous and nitrous acid require an appreciable time, and the best results are obtained by allowing the solution to stand about two minutes before the addition of the phenol. This, however, is not essential. Ten cc. of the phenol solution are now added as quickly as possible by blowing the solution from a pipette from which the tip has been removed.

The chlorine gas which remains in the flask above the liquid is removed by blowing into the flask, and the sides are washed down with a jet of water. If the solution is allowed to stand at this point nitrophenol will slowly form. Sodium hydroxide is therefore added until a very slight precipitate is obtained. The solution is now made acid with acetic acid; only a few drops should be required to dissolve the precipitate. Ten cc. of the potassium iodide are added, and the titration made with the standardised thiosulphate. If great accuracy is required the titration is finished with a weak solution of thiosulphate.

Some results obtained by the method described above are given in the accompanying table. The milligrams found and the error are calculated only to a point which is within the degree of accuracy of the apparatus used.

For the opportunity of carrying out this work I wish to thank Dr. N. B. Foster, and for assistance with the analytical work Mr. A. W. Thomas.—*Chemical Engineer*, xv., No. 1.

## A METHOD OF ANALYSING SOME COMMERCIAL GOLD ALLOYS.

METALS PRESENT: GOLD, SILVER, COPPER, AND OCCASIONALLY ZINC AND TIN.\*

By JAS. O. HANDY.

*Preparation of Sample.*

Use a sharp file. Remove particles of steel with a magnet. Weigh out 0.5 grm. of filings in a 4-ounce beaker. Add 50 cc. of aqua regia (40 HCl and 10 HNO<sub>3</sub>). Heat just to boiling for fifteen minutes, or until decomposed. The AgCl is almost all dissolved when boiled with the strong acid. Boil down to 10 cc., add 25 cc. HCl, and again boil down to 10 cc., or until the AgCl begins to separate.

*Silver.*

Dilute to 150 cc. with water. Boil until the AgCl coagulates well. Cool, let stand until clear. Filter on a weighed paper, and wash the AgCl. Dry and weigh. (AgCl  $\times$  0.7527 = Ag.)

*Zinc.*

Add sufficient HCl to the filtrate to make 5 per cent of concentrated HCl by volume. Pass H<sub>2</sub>S through the cold solution rapidly for fifteen minutes. Filter and wash with H<sub>2</sub>S water. The filtrate contains only the zinc. Boil off H<sub>2</sub>S and precipitate with Na<sub>2</sub>CO<sub>3</sub>. Boil for fifteen minutes. Filter and wash with hot water. Dry, burn off in porcelain, and weigh ZnO after blasting. (ZnO  $\times$  0.8034 = Zn.)

*Tin.*

For the separation of Sn from Au and Cu in the sulphide precipitate we take advantage of its solubility in HCl. The precipitate (and filter paper) is placed in a beaker and covered with 50 cc. of a mixture of water (35 cc.) and HCl (15 cc.). Boil for ten minutes. Cool. Filter. Add HCl to make 25 per cent of concentrated acid by volume. Pass H<sub>2</sub>S to re-precipitate any dissolved Cu. Filter and wash with H<sub>2</sub>S water. Neutralise filtrate with ammonium

\* Paper read at the Indianapolis Meeting of the American Chemical Society before the Industrial Section.



hydroxide. Acidify with 1 cc. of HCl. Pass H<sub>2</sub>S to precipitate the Sn. Filter. Wash with H<sub>2</sub>S water. Burn off in a porcelain crucible, igniting finally over a blast. Weigh SnO<sub>2</sub>. (SnO<sub>2</sub> × 0.788 = Sn.) The CuS recovered as above is converted into CuO, and is then dissolved in 5 cc. of concentrated HNO<sub>3</sub> by warming. Any SnO<sub>2</sub> present is recovered and weighed, the amount being added to that already obtained. The Cu solution is added to that recovered from the gold by the next operation.

### Copper.

Burn off the sulphides of gold and copper in a porcelain crucible, avoiding a heat greater than that required to burn off the filter paper. This hinders the shrinkage of the metallic gold, and leaves it more porous, so that the CuO is readily dissolved out. Too high a heat causes CuO to unite with the glaze of the crucible. Place the Au and CuO mixture in a 4-ounce beaker. Add 10 cc. of concentrated HNO<sub>3</sub>. Boil for ten minutes. Add 3 cc. of concentrated H<sub>2</sub>SO<sub>4</sub>, and boil until the HNO<sub>3</sub> is all expelled and SO<sub>3</sub> fumes are coming off freely. Cool, add 50 cc. of water and 5 grms. sodium acetate. Boil and filter off the gold (the gold residues are weighed as an approximate check, and are saved for their commercial value only; gold is best determined by fire assay). Cool the filtrate and add 5 grms. of potassium iodide; stir until dissolved. Titrate with decinormal hyposulphite of sodium: 1 cc. = 0.0063 gm. Cu.

### Gold.

Scorify 0.5 gm. of filings with 40 grms. of test lead, 1 gm. of borax glass, and 1 gm. of powdered silica. The borax and silica flux are placed on the mixture of alloy filings and test lead. If the lead button resulting from scorification is hard repeat the scorification, adding 10 grms. more test lead and 2 grms. of borax and silica flux. Cupel carefully and weigh Au plus Ag.

The determinations previously made make it possible to calculate quite closely the amounts of Au and Ag, &c., in the alloy.

We make up a mixture containing the same metals in approximately the same proportions; 0.5 gm. of this "control" mixture is then scorified and cupelled side by side with an equal weight of the alloy. After weighing the gold and silver buttons from the assay and the "control," they are alloyed separately with 3 parts of pure Ag.

The alloys must be thoroughly melted in order to insure homogeneity. Flatten the buttons by hammering or rolling.

Part with HNO<sub>3</sub> of graded strengths as is the usual assaying practice. Boil well with water, dry, ignite, and weigh Au. Deduct Au from Au plus Ag; the difference is Ag. Increase both Au and Ag figures by the amounts of loss shown by the Au and Ag used in the "control" assay. The fire assay for Au and Ag yields in most chemists' hands the highest and the most accurate results. The correction for fire loss (volatilisation) is far higher for Ag than for Au. Gold alloys analysed by us had the following limits of composition:—

|                | Per cent.     |
|----------------|---------------|
| Gold .. .. .   | 48.0 to 99.50 |
| Silver .. .. . | 0.5 " 26.00   |
| Copper .. .. . | 0.0 " 18.00   |
| Zinc .. .. .   | 0.0 " 7.50    |
| Tin .. .. .    | 0.0 " 2.00    |

Those alloys highest in Ag were most difficult to dissolve in aqua regia.

We found the ratio 1 HNO<sub>3</sub> to 4 HCl most efficient. Aqua regia 1 to 3 was less efficient, and 1 to 2 very unsatisfactory. Increasing the percentage of HNO<sub>3</sub> in the mixture failed to cause more rapid solution, but increase of HCl produced unexpectedly rapid and complete decomposition.—*Journal of Industrial and Engineering Chemistry*, iii., No. 11.

## PROCEEDINGS OF SOCIETIES.

### CHEMICAL SOCIETY.

Ordinary Meeting, March 21st, 1912.

Prof. PERCY F. FRANKLAND, LL.D., F.R.S., President, in the Chair.

MR. W. J. S. NAUNTON was formally admitted a Fellow of the Society.

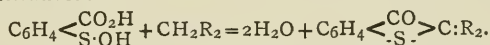
Certificates were read for the first time in favour of Messrs. Arthur Anderson Bones, 640, Schoeman Street, Pretoria, S. Africa; Raymond Edwin Crowther, Edenvale, Wigton Road, Carlisle; William Dallas, Burnbank Cottage, Mount Vernon, Glasgow; Archibald Knox, 18, Newhall Terrace, Greenhead, Glasgow; Edwin Charles Lacey, B.Sc., St. Julian's Lodge, West Norwood, S.E.; Leslie Herbert Lampitt, M.Sc., Bowyer Road, Saltley, Birmingham; Robert John Milbourne, Muxton Lodge, Newport, Salop; George Walker, Stonehurst, Lancaster Road, Morecambe; Charles Reginald Wilkins, B.Sc., 40, Church Lane, Hornsey, N.

A certificate has been authorised by the Council for presentation to ballot under By-law I. (3) in favour of Mr. John Scott Thomson, Crawford Street, Dunedin, N.Z.

Of the following papers those marked \* were read:—

\*56. "Syntheses of 3-Oxy-(1)-thionaphthen." By ARCHIBALD MORITZ HUTCHISON and SAMUEL SMILES.

It was shown that in the presence of concentrated sulphuric acid and chlorosulphonic acid or other similar reagents, *o*-thiol- and *o*-dithio-benzoic acids with malonic acid or ethylacetoacetate yield 3-oxy-(1)-thionaphthen or derivatives thereof. Reasons were given for considering that this reaction is caused by the condensation of the sulphylic acid (*Trans.*, 1911, xlix., 640) with these methylene derivatives:—



It was also pointed out that other examples of this type of interaction are to be found in technical processes for preparing "thioindigo."

\*57. "Behaviour of Metallic Alloys when heated in a Vacuum." By CLARENCE RICHARD GROVES and THOMAS TURNER.

The authors have heated a number of binary alloys in a porcelain boat under a pressure not exceeding 1 mm. of mercury. The boat was contained in a porcelain tube, and heated in an electric resistance furnace to temperatures ranging from 500° to 1200°.

It is concluded that the alloys may be divided into five groups as follows:—

1. The metals are not appreciably volatile when heated in a vacuum for a moderate time at or below 1200°.

As examples of this class may be mentioned the alloys of copper with iron, aluminium, tin, or nickel. It may also be assumed that any mixtures of these four metals in any proportions would also be non-volatile.

2. The constituent metals are quantitatively separable.

Thus the alloys of the copper-bismuth, copper-lead, and copper-zinc series all separate at the melting-point of copper. The bismuth, lead, or zinc volatilise, whilst pure copper remains. Iron-zinc alloys can be quantitatively separated at 500°.

3. Any excess of the more volatile metal is removed, and a chemical compound remains.

The gold-zinc series yields AuZn; the copper-antimony, Cu<sub>3</sub>Sb; the gold-cadmium, AuCd; and the magnesium-zinc, MgZn<sub>2</sub>.

4. The excess of the more volatile metal is removed, but the residue is not a chemical compound.

Thus in the copper-arsenic series the arsenic retained diminishes as the temperature rises. At 1200° the com-

position remains constant with about 20 per cent of arsenic, which does not correspond with any simple atomic proportions.

5. Two (or more) metals may volatilise together.

Thus lead and zinc tend to pass over together. In the iron-zinc series also there is an increasing proportion of the iron carried over as the temperature rises from 500°. In the silver-zinc series, although separation is nearly quantitative at 700°, there is an increased loss of silver with higher temperatures.

#### DISCUSSION.

Dr. HODGKINSON inquired if the authors had observed any gas evolution during the process, although he doubted whether that would have been possible owing to the character of the vacuum which had to be maintained against a sealing-wax closure.

His reason for asking was that recently he had melted some very pure electrolytic copper in a silica tube in a Sprengel vacuum, and the evolution of hydrogen had not ceased when the tube cracked after more than twelve hours' heating. The globule of copper was found to be full of large bubbles when cut open after cooling.

The total separation of zinc from copper in brass at 1100° in a vacuum appeared very extraordinary, as some eight or nine years ago he, with Major Howarth, R.A., had made brass of the composition  $\text{Cu}_2\text{Zn}$  by passing zinc vapour, with the aid of a stream of hydrogen, over copper heated to a little over 1000°.

Other metals, such as platinum, nickel, and palladium, also retained definite amounts of zinc in similar circumstances.

Dr. J. F. SPENCER pointed out that Prof. Turner's experiments indicated that alloys could be divided into pairs, depending on their behaviour on distillation, which were analogous to the various pairs of completely miscible liquids; thus, for example, with some of the alloys a complete separation was possible, whilst with others one metal distilled away, leaving apparently a definite compound. This supposed compound corresponded exactly with the constant-boiling liquid mixture of minimum vapour pressure. Dr. Spencer asked the author if he had made any experiments to see if the composition of the supposed compound was changed in any way, for example, by change in the pressure under which the distillation was carried out.

Mr. EGERTON drew attention to the construction of the electric resistance furnaces used by Prof. Guntz in his work on the preparation and distillation of metallic barium, and asked Prof. Turner whether he had had trouble with the platinum at high temperatures. Another point which had interested him was the mention of the vapour pressure of metals at the ordinary temperature; it was questionable whether a crystalline metal had any vapour pressure below a certain temperature.

Mr. W. P. DREAPER suggested that the results should be extended to 1300°, so that they could be compared with those recently obtained by Sir W. Crookes, where even iridium lost 7 per cent of its weight on heating for twenty-two hours. If the iron-copper alloys were stable at that temperature, it would be an interesting fact.

Prof. TURNER said, in reply to Dr. Hodgkinson, that their experiments showed that the quantity of gas evolved with the relatively small quantities of alloys employed was usually small. When any considerable quantity of gas was evolved, they found that some was occluded in the tube, but practically the whole of this was evolved if the tube were cooled and re-heated. With a second cooling and re-heating, the residue of gas was very small indeed. Porcelain tubes were less permeable to gases at high temperatures than fused silica tubes. It was possible to make brass by heating bright copper in an exhausted glass tube containing zinc at a temperature 50° below the melting-point of zinc, or, say, 375°. The platinum in the resistance furnace was in the form of a spiral of thin sheet. It lasted well so long as the temperature did not exceed 1200°, but deteriorated rather rapidly with greater heat.

No doubt if some of the alloys examined had been subjected to a higher temperature, different and very interesting results might have been obtained. He hoped someone would carry out such experiments. The separation of metals in a vacuum was usually effected at the melting-point of the less fusible metal, but in some cases, as in the zinc-iron series, the alloy was solid throughout the experiment. They had tried various substances for making the joints at the cold ends of the porcelain tube, and had found ordinary red sealing-wax gave the most satisfactory results.

\*58. "*Oxidation of Atmospheric Nitrogen in Presence of Ozone.*" By THOMAS MARTIN LOWRY.

When air under the ordinary pressure is driven over a series of spark-gaps a product is obtained which gives an increased yield of nitrogen peroxide if mixed with ozone. It is suggested that this product may contain a chemically active form of nitrogen.

#### DISCUSSION.

Dr. FEILMANN remarked that it would be comparatively easy to test Dr. Lowry's hypothesis on the formation of active nitrogen by passing pure nitrogen, free from oxygen, over a spark-gap, and then mixing it with ozonised air.

Dr. ROBERTSON stated that in extending the spectroscopic method for the quantitative estimation of nitrogen peroxide to mixtures containing that gas in very low concentrations, he had found it advisable to make the parts of the apparatus of non-reactive substances; thus for strict quantitative work, observation tubes should be made of silica rather than of glass.

\*59. "*Method of Producing a Steady Thallium Flame.*" By THOMAS MARTIN LOWRY.

Thallium chloride is vaporised by heating it gently in a silica bulb, and is carried into the flame by a current of oxygen. The oxygen is admitted to the bulb by a horizontal tube, and passes into the flame through a second tube, which terminates in a vertical jet.

\*60. "*Electro reduction of Alkyl Nitrosoamides.*" By HILMAR JOHANNES BACKER.

In continuation of previous researches on the electro-reduction of nitrosoamino-compounds to hydrazines (Diss., Leyden, 1911), the author has studied the reduction of alkyl nitrosoamides of common organic acids, which has been unsuccessfully attempted by various investigators.

It was shown that *oxalylbismethyl nitrosoamide* (m. p. 66°, decomp.) and *succinylbismethyl nitrosoamide* (m. p. 110°, decomp.), when reduced in slightly acid solution with a tinned cathode, yield the corresponding hydrazides, which may be isolated as benzylidene derivatives.

The above-mentioned nitrosoamides, especially that of oxalic acid, are unstable. Their decomposition by alkalis and organic bases was described; in each case diazomethane is formed.

\*61. "*Model of an Asymmetric Carbon Atom.*" By WILLIAM EDWARD GARNER.

The author has constructed a model to illustrate the explanation, proposed by Werner ("*Lehrbuch der Stereochemie*," 1904, 49), of the racemisation of optically active compounds.

The asymmetric carbon atom is represented by a cube, which is composed of four wooden blocks ( $\frac{3}{4}'' \times \frac{3}{4}'' \times 1\frac{1}{4}''$ ). The blocks are placed vertically, and bolted in a horizontal direction, leaving a space of  $\frac{1}{4}''$  between the blocks (Fig. 1). The bolts are placed as near the centre of the model as possible. Fig. 3 gives a cross-section, showing the manner in which the bolts are employed. Four iron rods are attached to the bolts in such a way that they can move freely in a vertical direction. Each rod is connected to the two adjacent rods by thin cord, which passes through rings at the top and the bottom of the cube. The method by which this is accomplished may be seen by reference to the diagram (Fig. 2). This represents the top of the cube, but the arrangement of the cords which pass through the lower ring is similar to this if the model be viewed from underneath.



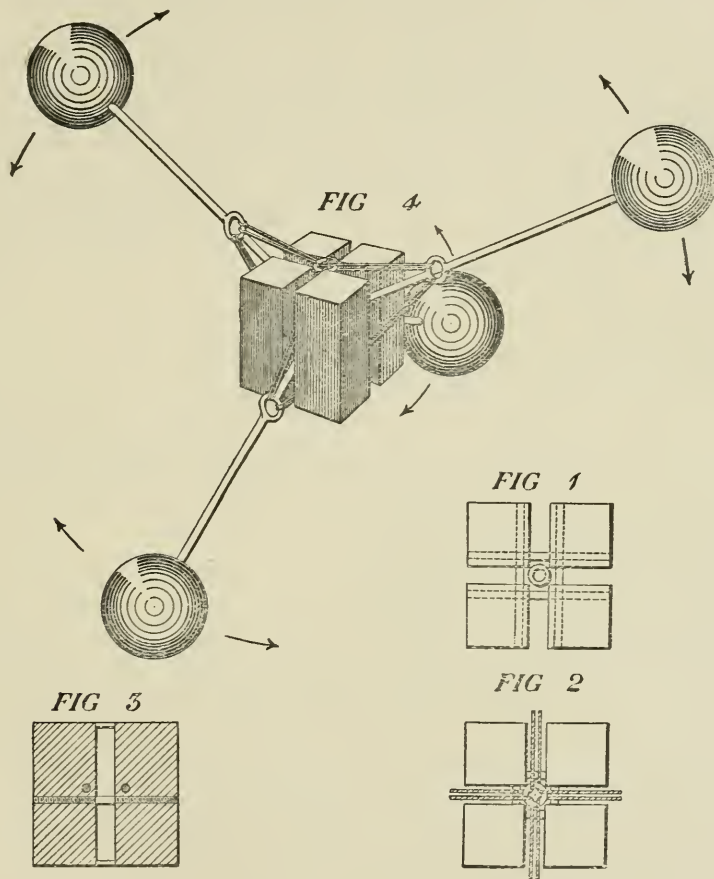
With such a method of attachment, when one arm is vibrated in a vertical direction, all the others move in unison. If one is moved in an upwards direction, then the two adjacent rods will move downwards, whilst that in the opposite position will move upwards (Fig. 4).

Differently coloured balls are attached to the arms, and a model of the asymmetric carbon atom is obtained. If the balls are placed in the order shown in the diagram (Fig. 4), then the arrangement is that of an optically active compound, and if they occupy the vertices of a tetrahedron, the model now illustrates the van't Hoff conception of the asymmetric molecule.

The views of Werner may be illustrated by moving one of the balls up and down, thus causing the other balls to vibrate. This is taken to be the normal condition of the molecule. The application of some external strain, for

The difficulty with which cyclic compounds racemise may be illustrated by tying two opposite arms together, and re-adjusting the lengths of the strings which control the movement of the arms. It is difficult to bring the other two arms into the plane containing the asymmetric carbon atom, since one of the balls must occupy a position within the ring. For a new arrangement to be formed this ball must pass through the ring, and this is presumably impossible if the group contains several atoms; thus the racemisation of a cyclic compound is practically impossible, unless it can take place through the formation of an intermediate compound.

Whilst the model does not explain the Walden inversion, it is useful in dealing with this process. In the model, only the simplest case can be represented, namely, that in which the amplitude of the vibration of all groups



example, application of heat, causes an increase in the amplitude of the vibration of the groups until all lie in one plane for a small interval of time. This arrangement of the balls is not asymmetric, since a plane of symmetry can be drawn through the carbon atom. Once the balls are in this position there is an equal chance of their returning into their old arrangement or of passing into a new arrangement, which is the mirror image of the first; thus a ball, moving downwards, may continue its movement through the plane of racemisation, and vibrate about a new mean position. This change is similar to that which occurs in the so-called Walden inversion of optically active compounds. Since the new form so produced is transformed with the same facility into the old form, the model gives a method of illustrating Werner's view of racemisation.

is the same, but this will not interfere with its use for purposes of demonstration.

Another application of the model is to illustrate a possible explanation of the effect of the solvent on the rotation of an optically active compound. The diminution of the rotation is thus represented by moving the arms nearer to the plane of racemisation, and imparting a motion to them in this new mean position. The model may be used similarly to demonstrate in accordance with the above theory the changes in the rotation of an active compound with temperature.

The re-adjustment of the strings connecting the arms will serve as a means of altering the valency directions, and so illustrate what may take place when one group is sub

stituted by another. This will alter the direction of the plane of racemisation.

The conversion of fumaric acid into maleic acid may be illustrated by employing two models, in which two adjacent bonds of each are united by short pieces of indiarubber tubing. The groups are then arranged so that the combined model represents either maleic or fumaric acid. If the groups attached to each carbon atom be made to vibrate with the same amplitude, the particular form will be retained; but if the groups attached to one carbon atom be made to pass the plane of racemisation, then the other form is produced.

(We are indebted to the Chemical Society for permission to reproduce the accompanying illustrations).

\*62. "Organic Derivatives of Arsenic and Antimony." (Preliminary Note). By GILBERT T. MORGAN and FRANCES M. G. MICKLETHWAIT.

The Grignard reaction carried out with benzyl chloride and antimony trichloride leads to the production of *tribenzylstibine dichloride* (m. p. 105–108°), lustrous crystals, from alcohol; this is hydrolysed to *tribenzylstibine oxide*, which decomposes indefinitely at 240°. Other products of this condensation are being examined.

Comparative experiments with arsenic trichloride and benzyl chloride have shown that the Grignard condensation leads to derivatives of quinquivalent arsenic, from which tribenzylarsine oxide has been obtained.

Antimony trichloride has also been condensed under Grignard conditions with *m*-bromotoluene, *p*-dibromobenzene, *p*-iodonitrobenzene, 4-iodo-1:3-dinitrobenzene, and the three isomeric iodoanilines.

These experiments are being continued with the object of preparing asymmetric organic derivatives of arsenic and antimony suitable for resolution into their optically active components.

63. "isoErucic Acid." By ALEXANDER KILLEN MACBETH and ALFRED WALTER STEWART.

In the course of some investigations of absorption spectra, the authors had occasion to purify brassidic acid, two specimens of which were obtained from Schuchardt. This acid was re-crystallised about fifteen times from alcohol, and had a sharp melting-point (60°), which remained unchanged by the repeated re-crystallisations. On boiling it finally with animal charcoal, the melting-point was found to fall to 57–57.2°, and remained constant at this after further re-crystallisations. The absorption spectrum of the substance was examined, and found to show slightly less general absorption than either erucic or brassidic acid. Similar results are obtained if crude brassidic is used instead of the purified sample.

An examination of the substance shows that it is unsaturated, as it is easily brominated in aqueous suspension, yielding a bromine derivative (m. p. 46–46.6°). This substance appears to be the dibromide of *isoerucic acid* (m. p. 42–43°), for the dibromide of brassidic acid melts at 54°. *isoErucic acid* itself is stated to melt at 54–56°, so that it appears probable that the substance obtained as described above is *isoerucic acid* in a purer form than has hitherto been produced.

The suggestion has been put forward in the case of oleic acid that the existence of the third isomeride is to be explained by assuming that in *iso*-oleic acid the double bond has been shifted into the  $\alpha$ -position with regard to the carboxyl group. If the same idea is applied to *isoerucic acid*, we should expect to find its absorptive power to be greater than either that of brassidic or erucic acids, owing to the presence of a pair of conjugated double bonds in the molecule; but since it has actually less absorption than either of the other isomerides, this explanation of the isomerism cannot be applied to the present case.

It is proposed to examine other cases of the kind with the view of determining whether the method is generally applicable to the preparation of these *iso*-forms.

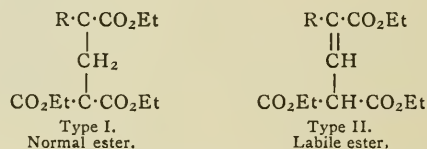
64. "p-Hydroxystilbene and its Derivatives." By JOHN THEODORE HEWITT, WILLIAM LEWCOCK, and FRANK GEORGE POPE.

The analogy existing between derivatives of azobenzene, benzylideneaniline, and stilbene has been extended by the preparation of 4-hydroxystilbene and its 4'-nitro-derivative, and comparison of their absorption spectra in neutral and alkaline solution with those of stilbene and 4-nitrostilbene. The corresponding methoxy-compounds have also been examined.

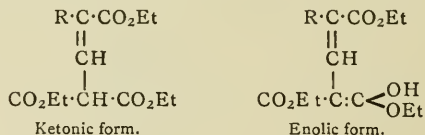
4-Hydroxystilbene is colourless, but shows a strong absorption band in the ultra-violet; a band which is partly in the visible region of the spectrum is shown by the 4'-nitro-derivative. Addition of alkali to the alcoholic solutions of both compounds causes the band to shift towards the red end of the spectrum, but the displacement is considerably greater in the case of nitrohydroxystilbene than in that of hydroxystilbene itself.

65. "The Chemistry of the Glutaconic Acids. Part V. The Esters of Substituted Glutaconic Acids." By NORMAN BLAND and JOCELYN FIELD THORPE.

It was shown that the esters of substituted glutaconic acids having two negative groups attached to the same carbon atom yield enolic sodium derivatives which dissociate in water to an extent depending on the tendency for the hydrogen atom to pass back into the three-carbon system. The esters formed in this manner are the normal esters of type (I.). The undissociated sodium compounds then yield the labile esters (type II.) when decomposed by carbon dioxide:—



The esters of type II. may exist in either their ketonic or enolic forms:—



and it was shown that the stability of these forms depends on the nature of R.

Thus when R = methyl, the ketonic form is alone capable of existence in the free state; whereas when R = benzyl, an equilibrium mixture of the two desmotropic individuals is produced.

When a methyl group occupies the  $\beta$ -position and a benzyl group the  $\alpha$ -position, tautomerism ceases to be apparent, and the ketonic and enolic forms becomes structurally distinct.

66. "Viscosity of Compounds containing Tervalent Nitrogen. Part I. The Amines." By ALBERT GEORGE MUSSELL, FERDINAND BERNARD THOLE, and ALBERT ERNEST DUNSTAN.

Forty-four amines have been examined in the pure state at 25° and 130°, also in amyl acetate and in hydrochloric acid solution. Viscosities have been expressed in terms of the quantity  $(\eta + 10^6)/\text{Mol. vol.}$ . The order of increasing viscosity is tertiary, secondary, primary.

Substitution of an alkyl group for hydrogen lowers the molecular viscosity. Substitution of an acyl, phenyl, or benzyl group for hydrogen increases the molecular viscosity. Substances with a very high value of K have correspondingly high viscosities.

There is a close parallelism between the association constant  $\alpha$  and molecular viscosity. Meta-compounds have, in general, lower viscosities than ortho- or para-



derivatives. Conjugation of unsaturated groupings increases viscosity, and acts in a similar way on K.

67. "Reciprocal Influence of Unsaturated Centres and its Effect on the General Absorptive Power of Compounds." By ALEXANDER KILLEEN MACBETH, ALFRED WALTER STEWART, and ROBERT WRIGHT.

From an examination of the absorption spectra of various stereoisomerides, the authors find that if a molecule contains an unsaturated centre U, such as a carboxyl group, and a saturated centre S, such as an alkyl radicle, a variation in the relative spatial positions of S and U produces very little change in the general absorptive power of the molecule. On the other hand, if the molecule contains two unsaturated centres, a change in their relative spatial positions produces a marked alteration in the absorption spectrum; thus erucic and brassic acids have very similar absorption spectra, whereas the spectra of maleic and fumaric acid differ very considerably from each other. From this the authors deduce that in order to alter the general absorptive power of a molecule it is necessary to change the relative positions of at least two unsaturated centres within the molecule. The action of two centres of unsaturation is also shown by a comparison of the absorption spectra of ammonium thiocyanate and thiocarbamide. In the former there is only one unsaturated centre, namely, the 'CNS-group'; whilst in the latter there are two, namely, the amido-radicles. The latter compound has a much greater absorptive power than the former.

68. "Experiments on a Yellow Colouring Matter from Ergot." By ALBERT FREEBORN.

It was shown that the three yellow colouring matters hitherto obtained from ergot (sclerocrystallin, ergochrysin, and secalonic acid) are in all probability identical, and have the composition  $C_{21}H_{22}O_9$ . Another substance, crystallising in pale yellow needles, of the composition  $C_{17}H_{14}O_7$ , and melting at  $338^\circ$ , has now been obtained. It yields a tetra-acetyl derivative,  $C_{23}H_{20}O_{10}$ , melting at  $231^\circ$ , and does not contain methoxyl. On fusion with potassium hydroxide, an unidentified phenolic acid is formed, probably containing at least three phenolic hydroxyl groups.

69. "Density of Acetic Acid. A Correction." By WILLIAM ROBERT BOUSFIELD and THOMAS MARTIN LOWRY.

In the paper on acetic acid (Bousfield and Lowry, *Trans.*, 1911, xcix., 1439) the difference in the density of acetic acid for  $1^\circ$  was given as 0.00123 instead of 0.00113. This does not affect the data given in the paper, but introduces errors of 0.0001 to 0.0003 in the reduction to  $18^\circ$  of the values given by other observers.

## SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, April 3rd, 1912.

MESSRS. Maurice E. Balston, Howard A. Caulkin, and Charles Reginald Wilkins were elected members of the Society.

Certificates were read for the first time in favour of Messrs. Harold Thomas Cranfield, Midland Agricultural and Dairy College, Kingston, Derby; Ernest Gabriel Jones, 36, Dansie Street, Liverpool; and William Henry Roberts, 36, Dansie Street, Liverpool.

Certificates were read for the second time in favour of Messrs. Reginald Freeman Easton and Leonard Goodban.

The following papers were read and discussed:—

"Note on the Milk of a Small Herd." By EDWARD RUSSELL.

This paper deals with the composition of the milk of a small herd collected in September, 1911, and shows how the abnormal meteorological conditions affected the composition of the milk as regards non-fatty solid matters.

"A Distillation Method for Separating Arsenic from Antimony and other Metals, and its Application to Toxicological Work." By STANLEY W. COLLINS.

This method depends on the volatilisation of arsenic in the vapour of methyl alcohol and a stream of hydrogen chloride (compare *Ber.*, 1895, xxviii., 1414), sulphuric acid being added in sufficient quantity to retain the more basic antimony. Compounds containing pentavalent arsenic are reduced by an excess of ferrous chloride before distillation. The method has been applied to the separation of arsenic from organic matters, including such small amounts as would be present in toxicological work. As an example of this, estimations of arsenic have been made in the viscera from a case which had been treated with Salvarsan.

"Estimation of Ferric Iron in presence of Organic Matter." By JOHN THEODORE HEWITT and GLADYS RUBY MANN.

The authors find that ferric iron can be estimated in presence of organic matter by means of thiosulphate (Scherer, Kremer and Landolt, Oudemanns, F. Mohr, Braun, Joseph, Schatz). Three cc. of 1 per cent copper sulphate and 1 cc. of 1 per cent ammonium thiocyanate are added; N/10 sodium thiosulphate run in until the colour of the ferric thiocyanate is discharged, and the excess of thiosulphate determined by iodine and starch. Useful results were obtained in presence of alcohol, acetic, tartaric, and citric acids, phenol, and various carbohydrates.

"The Relation of the Kirschner and Polenske Values in Margarine containing Palm Kernel or Coconut Oils." By E. RICHARDS BOLTON, H. DROOP RICHMOND, and CECIL REVIS.

The Kirschner values for margarine containing coconut or palm kernel oil with or without butter-fat up to and including 10 per cent, may be represented by straight line curves for percentages between and including 5 and 75 per cent of these two fats. The presence of butter-fat displaces the curve laterally and practically parallel to the "no-butter" Kirschner curve, proportionately to the butter-fat present.

The Polenske value for margarines containing these fats is practically independent of the presence of butter-fat up to and including 10 per cent, so that a mean value Polenske curve may be drawn which will be true for all mixtures, and acts as an "indicator value" determining the content of coconut or palm kernel oil in all cases. The curve is parabolic and the equations are given together with equations for estimating the amount of butter-fat from the Kirschner and Polenske values determined. A tentative relation between the Kirschner and Polenske values for butter-fat is given.

"A convenient Apparatus for obtaining an Average Sample of Gas and for Regulating the Flow of a Gas into an Evacuated Vessel." By FRANK STURDY SINNATT.

The apparatus consists of a gradually diminishing and adjustable mercury seal. The gas to be collected is forced to flow through the column of mercury. By this means samples of gases may be taken from any source at a constant rate, being collected in an evacuated vessel. The apparatus will find application in the obtaining of representative samples of gas over extended periods of time, as it requires practically no attention. The latter is a valuable feature, as other continuous sampling devices are not so simple nor so accurately adjustable.

Comparative Hydrolysis of Saccharose by Different Acids in presence of Sucrose.—Gabriel Bertrand and M. and Mme. Rosenblatt.—In the case of peroxydiastase, sucrose, and doubtless of many other soluble ferments, it appears that in presence of the specific colloidal substance of complementary activity, the activity of different acids does not depend only on the hydrogen ions which are due to their electrolytic dissociation, but also upon the nature of the radicles or anions to which the hydrogen is attached in the acid molecule.—*Bull. Soc. Chim. de France*, xi.-xii., No. 4.

## OBITUARY.

DR. EDWARD DIVERS.

It is with much regret that we announce the death at his London residence of Dr. Edward Divers, M.D., D.Sc., F.R.S.

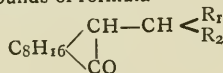
Dr. Divers was born in London in 1837; he received his early education at the City of London School, and subsequently studied at the Royal College of Chemistry and at Queen's College, Galway. After holding the post of Lecturer on Medical Jurisprudence at the Middlesex Hospital Medical School for three years, in 1873 he was appointed Professor of Chemistry at the Imperial College of Engineering in Japan, and became the Principal of the College in 1882. He was Vice-President of the Chemical Society from 1900 to 1902, President of the Chemical Section at the British Association Meeting of 1902, Vice-President of the Institute of Chemistry in 1905, and President of the Society of Chemical Industry in the same year. He was elected a Fellow of the Royal Society in 1885, and received the Second Class of the Order of the Sacred Treasure and the Third Class of the Order of the Rising Sun in recognition of his services to scientific education in Japan.

Dr. Divers' chemical work lay almost exclusively in the region of inorganic chemistry, and he was the author of many scientific papers, some of which were written in collaboration with his Japanese students. The compounds of nitrogen and oxygen were made the special subject of his study, and he published papers on the nitrites, the decomposition of hyponitrous acid and of its silver and mercury salts, and the existence and formation of salts of nitrous oxide. He investigated the constitution of nitrogen tetroxide, of the nitrososulphates of barium and lead, and of calcium sulphate, and also analysed many Japanese ores. In collaboration with Mr. T. Haga he studied the constitution and properties of nitrosulphonic acid, the preparation of hydroxylamine sulphate, and the reduction of nitrites to hydroxylamine, and with Mr. Kawakita published an account of the chemistry of the fulminates. Dr. Divers did some valuable work in the investigation of selenium and tellurium, and worked out a method of separating the two elements.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. cliv., No. 7, February 12, 1912.

Derivatives of Menthone.—Eyvind Boedtker.—By the action of alkyl magnesium bromides upon benzylidene-menthone compounds of formula—



may be obtained. The author has prepared thus menthomethylphenylmethane and menthoisoamylphenylmethane. Benzoylmenthone may be obtained by allowing benzoyl-chloride to act upon a solution of sodium menthone in toluene. The yield is poor.

Lactonisation of  $\alpha$ -Ketonic Ethers. Pyruvic Ether.—H. Gault.—The constitution attributed by Genvesse to the ether resulting from the action of HCl on ethyl pyruvate is improbable, and the author believes it to be an enol ethoxy ether of ketovalerolactone carbonic ether. The action would then be similar to that of hydrochloric acid on pyruvic acid, which gives rise exclusively to ketovalerolactone carbonic acid.

Action of Bromine and Chlorine on Dehydrodi-carvacrol.—H. Cousin.—Bromine reacts with dehydrodi-carvacrol to give a dibrominated derivative,  $\text{C}_{20}\text{H}_{24}\text{Br}_2\text{O}_2$ . Chlorine yields two different compounds, the dichlor

derivative analogous to the dibrom compound, and, with excess of chlorine, a product of formula  $\text{C}_{20}\text{H}_{22}\text{Cl}_2\text{O}_2 + 4\text{Cl}$ , which is a tetrachloride of dichlorodehydrodi-carvacroquinone.

## MISCELLANEOUS.

Iron and Steel Institute.—The Annual Meeting of the Institute will be held at the Institution of Civil Engineers, Great George Street, Westminster, on Thursday and Friday, May 9th and 10th, 1912, commencing each day at 10.30 o'clock a.m. The following is the list of papers that are expected to be submitted for reading and discussion:—

- "Notes on the Solubility of Cementite in Hardenite," by Dr. J. O. Arnold and L. Aitchison (Sheffield).
  - "Chemical and Mechanical Relations of Iron, Vanadium, and Carbon," by Dr. J. O. Arnold (Sheffield) and Prof. A. A. Read (Cardiff).
  - "Notes on a Bloom of Roman Iron from Corstopitum (Corbridge)," by Sir Hugh Bell, Bart. (Middlesbrough).
  - "Influence of Carbon on Corrosion," by C. Chappell (Sheffield).
  - "Manufacture and Treatment of Steel for Guns," by General L. Cubillo (Valladolid, Spain).
  - "Corrosion of Nickel, Chromium, and Nickel-chromium Steels," by Dr. J. N. Friend, J. Lloyd Bentley, and W. West (Darlington).
  - "Mechanism of Corrosion," by Dr. J. N. Friend, W. West, and J. Lloyd Bentley (Darlington).
  - "Sinhalese Iron and Steel of Ancient Origin," by Sir Robert A. Hadfield, F.R.S. (Sheffield).
  - "Modern Rolling-mill Practice," by J. W. Hall (Birmingham).
  - "Influence of Heat on Hardened Tool Steels," by E. G. Herbert (Manchester).
  - "Improvements in Electric Steel Furnaces and their Application in the Manufacture of Steel," by Dr. H. Nathusius (Friedenshütte, Upper Silesia).
  - "New Process for the Investigation of Fractured Surfaces of Steel," by F. Rogers (Sheffield).
  - "Welding up of Blowholes and Cavities in Steel Ingots," by Dr. J. E. Stead, F.R.S. (Middlesbrough).
  - "Note on some Remains of Early Iron Manufacture in Staffordshire," by Prof. T. Turner (Birmingham).
- The date and place of the Autumn Meeting will be announced at the Annual Meeting.—G. C. LLOYD, Secretary.

## MEETINGS FOR THE WEEK.

- TUESDAY, 23rd.—Royal Institution, 3. "Algernon Charles Swinburne—His Early Life and Work," by Edmund Gosse, LL.D.
- Faraday Society, 8. General Discussion on "Magnetic Properties of Alloys." (See p. 180).
- WEDNESDAY, 24th.—Royal Society of Arts, 8. "Technical Education in Ireland," by G. Fletcher.
- THURSDAY, 25th.—Royal Institution, 3. "Synthetic Ammonia and Nitric Acid from the Atmosphere," by Prof. A. W. Crossley, F.R.S.
- Royal Society of Arts, 4.30. "The Central Provinces," by Sir John O. Miller, K.C.S.I.
- Royal Society. "Diffusion and Mobility of Ions in a Magnetic Field," by J. S. Townsend. "Observed Variations in the Temperature Coefficients of a Precision Balance," by J. J. Manley. "The Torque produced by a Beam of Light in Oblique Refraction through a Glass Plate," by Dr. Guy Barlow. "Contributions to the Study of Flicker," by Dr. T. C. Porter.
- FRIDAY, 26th.—Royal Institution, 9. "Sir William Herschel," by Sir George H. Darwin, K.C.B., &c.
- Physical, 5. Adjourned Discussion on Mr. H. Donaldson's paper on "The Coefficients of Expansion of Fused Silica and Mercury." "Solution of Net-work Problems by Determinants," by R. Appleyard. "Method of Measuring Small Inductances," by S. Butterworth.
- SATURDAY, 27th.—Royal Institution, 3. "The Architecture of the Renaissance in France," by Reginald Blomfield.



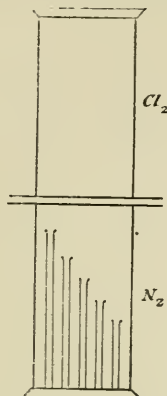
# THE CHEMICAL NEWS.

Vol. CV., No. 2735.

## APPARATUS TO STUDY THE DIFFUSION OF CHLORINE GAS.

By W. R. FORBES, B.Sc.

THE upper jar contains chlorine and the lower nitrogen. In the lower jar a small wooden stand is placed containing a row of glass tubes of gradually decreasing height. These tubes are filled with a solution of starch and potassium iodide. As the chlorine diffuses it gradually



liberates the iodine in the series of tubes, which gives with the starch the usual blue coloration.

By this means the diffusion of chlorine can be demonstrated to a large audience.

## THE INTERACTION OF GASEOUS MOLECULES.

By STANLEY SMITH.

It is well known that when two gases combine together they do so in some definite proportion, and that if a mixture of the two gases is taken in that proportion and combination effected, the resulting product will consist only of the compound formed by their union. If, however, a mixture be taken such that there is an excess of one gas above the amount required for the formation of the particular compound, then, after action has taken place, the residue consists of the compound of the two gases together with an uncombined residue of that gas which was originally present in excess.

The question therefore arises:—What is it that determines which molecules of the gas in excess enter into combination, and which are left unchanged at the end of the reaction.

If, for example, a mixture of  $N$  molecules of hydrogen and  $N$  molecules of oxygen be taken and union effected, then the product consists of  $N$  molecules of water together with  $N/2$  molecules of uncombined oxygen; the hydrogen molecules have thus in some way exerted a selective influence, and have combined with  $N/2$  molecules of oxygen, thus leaving a further quantity of  $N/2$  molecules of oxygen uncombined. What therefore is the factor that determines which of the molecules of oxygen shall enter into combination? There must have been in the original mixture some difference between the  $N/2$  molecules which have gone to form water and the  $N/2$  molecules which

remain. It does not seem possible that the selection can be of an arbitrary nature, and one therefore looks for an explanation.

Since it must be assumed that in a gaseous mixture the different molecules are equidistant from one another, it is impossible to afford an explanation on the basis that some of the molecules are more advantageously situated for combination than others.

The kinetic theory of gases, however, at once suggests a possible explanation; for since the molecules of a gas are moving with different velocities, and since combination depends on the number of impacts made between different molecules in a given time, then it follows that the molecules of a gas which are moving with the greater velocity will be those which enter into combination, while the molecules which are moving with the less velocity are left. This explanation at once suggests that the resulting residue should possess a lower temperature than would be anticipated, since the temperature of a gas depends on the mean velocity of its molecules.

It is possible that this phenomenon might be capable of experimental verification. Thus in one experiment two gases would be taken in combining proportions, and the temperature of the product taken after combination had taken place; in another experiment a mixture of the two gases would be taken such that there was an excess of one gas present above that required for the formation of the compound. Then if the temperature of the product is observed after interaction has taken place, and the value obtained corrected for dilution of the mixture, it would be expected that the latter temperature would be less than the former owing to the removal in one case of the molecules possessing the greater velocity. Again, the temperature might be observed after combination when the two gases are present in combining proportions, but diluted in one experiment with a certain volume of an inert gas, and diluted in another experiment with the same volume of one of the interacting gases. After due corrections have been applied the latter temperature should be less than the former value, owing to the fact that in the former experiment no selective removal of molecules can take place.

It is, of course, most probable that the difference in temperatures recorded would be very small; however, the kinetic theory of gases demands, or at least suggests, that some such difference should be found.

Chemical Department,  
University of Birmingham.

## RED WATER.

By JOHN E. MACKENZIE, D.Sc., Fh.D.,  
and  
T. M. FINLAY, M.A., B.Sc.

A SAMPLE of water sent by Dr. R. van Someren, Kystume SS., comp. by Kompola, Uganda, for analysis, has provided results which may be of some interest. In the letter accompanying the sample he says:—

"It comes from a crater lake out here, and I am very curious to know what gives it the red colour. The lake looks like blood at times. It seems to be saturated NaCl with some (?) lime."

The sample received had a distinct rose-pink colour. The bottle containing it was about three-quarters full of liquid, and a small amount of crystalline solid had separated, probably owing to evaporation and lowering of temperature.

The red colour was not separated from the water by filtration through ordinary filter-paper, but it was removed by means of a Berkefeld filter. On microscopic examination of the red deposit on the Berkefeld candle only disintegrated organic remains were seen. When mixtures of equal quantities of the water and nutrient agar were incubated at 25° and 30° C. there appeared on the sloped surface white growths of bacteria, which did not, however,

develop either in an artificially prepared brine of the same composition as the red water or in ordinary culture media. The colour disappeared on addition of mineral acid or caustic alkali. It was not extracted by ether. Its absorption spectrum showed several bands in the green and blue regions.

The following results were obtained by chemical analysis:—

|                          | Grms. per litre. |
|--------------------------|------------------|
| CO <sub>3</sub> .. .. .  | 58.6             |
| Cl .. .. .               | 154.9            |
| SO <sub>4</sub> .. .. .  | 36.4             |
| PO <sub>4</sub> .. .. .  | 1.6              |
| K .. .. .                | 5.5              |
| Na .. .. .               | 158.7            |
| SiO <sub>2</sub> .. .. . | Trace            |

The carbonic acid is present both as carbonate and bicarbonate, and the composition of the salts in solution may be given approximately as follows:—

|                                          | Grms. per litre. |
|------------------------------------------|------------------|
| Na <sub>2</sub> CO <sub>3</sub> .. .. .  | 96.8             |
| NaHCO <sub>3</sub> .. .. .               | 5.1              |
| NaCl .. .. .                             | 247.0            |
| KCl .. .. .                              | 10.5             |
| Na <sub>2</sub> SO <sub>4</sub> .. .. .  | 53.8             |
| Na <sub>2</sub> HPO <sub>4</sub> .. .. . | 2.4              |
| Total solids in solution ..              | 415.6            |

#### Analysis of Solid Residue.

|                         | Per cent. |
|-------------------------|-----------|
| CO <sub>3</sub> .. .. . | 29.1      |
| Cl .. .. .              | 10.9      |
| SO <sub>4</sub> .. .. . | 24.4      |
| K .. .. .               | 0.3       |
| Na .. .. .              | 35.3      |

And the probable composition as follows:—

|                                         | Per cent. |
|-----------------------------------------|-----------|
| Na <sub>2</sub> CO <sub>3</sub> .. .. . | 27.8      |
| NaHCO <sub>3</sub> .. .. .              | 18.5      |
| NaCl .. .. .                            | 17.0      |
| KCl .. .. .                             | 0.7       |
| Na <sub>2</sub> SO <sub>4</sub> .. .. . | 36.0      |

Twenty-five cc. of solution decolorised 10 cc. of N/10 KMnO<sub>4</sub>. No ammonia could be detected on boiling with alkali or with zinc-dust, and Ilosva's reagent only showed a very slight pink tinge after long standing.

The chemical composition of the water therefore gives no clue to the colouring matter, which is probably of organic origin, and produced by an organism capable of growing in a practically saturated alkaline brine.

We should be glad to know of the occurrence of similar red brines, and the causes of the coloration.

Chemistry Department,  
University of Edinburgh.

**Action of Alkaline Sulphites on Copper Salts.—H. Baubigny.**—When copper sulphate is treated with excess of alkaline sulphite, dithionous acid is formed. The red precipitate, which is produced by the action of heat, when washed and dried gives sulphurous gases with separation of copper and formation of copper sulphate. It contains the elements of copper sulphite, but the author has not been able to establish its composition, since cuprous sulphite undergoes alteration if it is not kept in an atmosphere of sulphurous gas. This red precipitate is a product of the decomposition of the double cuprous-alkaline sulphites in solution.—*Comptes Rendus*, cliv. No. 7.

## RECENT DEVELOPMENTS IN BAKELITE.\*

By L. H. BAEKELAND.

(Concluded from p. 183).

IN my former publications (Baekeland, *loc. cit.*) I have described also an intermediate product, B, the existence of which is of considerable importance for certain industrial applications, because, although being infusible and insoluble, it nevertheless possesses the property of softening if heated, and of welding and moulding under the combined action of heat and pressure.

There are several other ways of obtaining "C"; for instance, Lebach (Knoll and Co.) uses a base as a condensing agent, and mixes the so obtained "A" with a strong acid, and heats at a moderate temperature (see Lebach, U.S. P., 965,823).

"C" can also be produced by heating oxybenzyl alcohol with CH<sub>2</sub>O, or its equivalents (see Baekeland, *Journ. Ind. and Eng. Chem.*, i., No. 3). Or instead of starting from oxybenzyl alcohol, we may start from Novolak, and heat it with CH<sub>2</sub>O, or equivalent substances (see Baekeland, "On Soluble Fusible Resinous Condensation Products of Phenols and Formaldehyde," *Journ. Ind. and Eng. Chem.*, i., No. 8; Belgian Patent, 213,576, February 15, 1909). Delaire (see British Patent, 15,517, 1905) has already shown that the fusible soluble resins are anhydrides of phenol alcohols. This can easily be demonstrated by heating, preferably *in vacuo*, oxybenzyl alcohol in a test-tube at 160–170° C. Heating oxybenzyl alcohol, in presence of acid solutions, favours considerably the formation of these anhydrides, or saliretins, saligeno-saligenin, and similar products (Beilstein, *Organ. Chemie*, 1896, ii., 1109; R. Piria, *Ann. Chem.*, xlviii., 75; lvi., 37; lxxxi., 245; xcvi., 357; Moitessier, *Fahresbericht*, 1886, 676; K. Kraut, *Ann. Chem.*, clvi., 123; Gerhardt, *Ann. Chim. Phys.*, [3], vii., 215; F. Beilstein and F. Seelheim, *Ann. Chem.*, cxvii., 83; C. Schotten, *Ber.*, 1878, p. 784). I believe this explains to us why bodies of the Novolak type are more easily engendered in presence of acid condensing agents, provided the CH<sub>2</sub>O be not used in excess.

The intervention of condensing agents for the formation of fusible soluble resins of the Novolak type is not indispensable. This has been shown as far back as 1905 by Story (D. R. P., 308,449), who, by simply boiling an excess of phenol with formaldehyde *without any condensing agent*, and evaporating afterwards, has obtained a soluble fusible resin of the Novolak type. Lately, Aylsworth (Belgian Patent, 232,899) has confirmed this method in a somewhat more complicated way. All these fusible resins are simply anhydrides of the corresponding phenol alcohols. Their fusibility and solubility are augmented by the presence of small amounts of phenolic bodies. In my former publication "On Fusible Soluble Resinous Condensation Products of Phenols and Formaldehyde" (*Journ. Ind. and Eng. Chem.*, i., No. 8), I considered these bodies as definite compounds of saliretin products, with a small excess of phenol. More recent work on the same subject, the details of which are not yet ready for publication, compels me to abandon this interpretation. We have to deal here simply with physical mixtures in the form of colloidal solid solutions of saliretin products with very small quantities of phenols. These small amounts of phenol are retained stubbornly by the phenol alcohol anhydrides or saliretin products, forming therewith a solid solution; this accounts for the difficulty of their complete removal.

This makes the chemistry of this whole subject extremely simple. The fusible soluble resins of the Novolak type are merely the old known saligeno-saligenins, saliretins, or anhydrides of phenol alcohols, containing in some cases in solid solution a smaller or larger amount of phenols.

\* Read at joint meeting of New England Section, Am. Chem. Soc. and Soc. Chem. Industry, Boston, November 10, 1911. From the *Journal of Industrial and Engineering Chemistry*, iii., No. 12.



If, then, we take into consideration that I succeeded in making C by heating six molecules of oxybenzyl alcohol with at least 1 molecule  $\text{CH}_2\text{O}$  or its equivalent, and that the same result is attained by heating Novolak or other anhydrides of phenol alcohols with the required amount of formaldehyde, the explanation of a heretofore rather perplexing set of reactions becomes exceedingly simple.

Instead of directly preparing Solid A by starting with phenol and formaldehyde and a base, we can make it in two steps; first, prepare Novolak or any other saliretin products, and then melt and mix it with the polymers of formaldehyde, and thus obtain a variety of Solid A, practically identical to the Solid A obtained by direct action of phenol and formaldehyde in presence of a base. This solid A, by further action of heat, will then change into hard infusible insoluble "C."

The similarity of the Solid A thus prepared is even greater if, instead of using formaldehyde, we use a mixture of formaldehyde and ammonia, so as to accelerate the hardening process. In place of this mixture of formaldehyde and ammonia, we can use its preformed and direct equivalent, hexamethylenetetramine. However, in the latter case the amount of ammonia introduced into the mixture, with the required amounts of  $\text{CH}_2$  group, becomes much larger than strictly necessary, and on account of this as soon as the final hardening sets in this excess of ammonia is liberated.

If the temperature of such a hexamethylenetetramine mixture be raised above  $110^\circ \text{C.}$ , self-heating starts in, and the whole mass raises like a sponge while hardening; this on account of the sudden liberation of ammonia vapours. This phenomenon which I show you here is in direct contradiction with the statement of Mr. Aylsworth (see Aylsworth, Belgian Patent, 232,899, February 11, 1910). It is quite true that my method of using counterpressure in a hydraulic press, or otherwise, can easily be called into service here, so as to allow the use of the high temperature at which rapid moulding and hardening becomes possible. In this respect small amounts of fixed alkalis, like caustic soda, have decided advantages over ammonia, or hexamethylenetetramine, in as far as they do not exaggerate the tendency of forming gaseous products by the elimination of  $\text{NH}_3$ , which causes foaming and porosity during the application of heat in the hardening process.

The properties of Bakelite, its chemical constitution, and some of its industrial applications, have been so often described that I will dispense with a general repetition thereof. The fact that it only chars at relatively high temperatures, its infusibility, its hardness and tenacity, its resistance to physical and to most chemical agents, and its ease of manipulation, explain sufficiently its uses in the arts.

In my former publication on the subject I have insisted in order to better differentiate its properties from those of hard rubber and celluloid, that it lacks the flexibility of the two latter products, but I have found since then that my statements have been taken too absolutely, instead of in a comparative sense. Here is, for instance, a thin plate of Bakelite, which is flexible enough for many purposes, and which is, furthermore, quite strong, but you will notice that if I bend it in an exaggerated manner it suddenly will snap off and break in many small pieces. It resembles in this respect a thin plate of glass, but it is not so fragile and is more flexible. Thrown on a hard surface it will not break as easily as glass, and will rebound. Nevertheless, it cannot stand the seemingly endless bending of the very flexible varieties of celluloid. There is no difficulty whatever, by the introduction of some substances which produce colloidal solid solutions, to make Bakelite so soft and flexible that a rod thereof can be twisted around one's finger; but in introducing these extra matters many of the other excellent qualities of Bakelite are sacrificed to a considerable extent; for those applications where great flexibility is required rubber and celluloid answer, incomparably better, the purpose.

I found that we can enormously increase the practical

uses of Bakelite by incorporating it with structural fillers like fibrous or cellular bodies. The beneficial action of the latter is remarkable, and seems to consist mainly in modifying the shattering wave which develops whenever an object made of Bakelite is submitted to a violent shock. Some substances, like rubber or celluloid, are weakened if they are mixed with large amounts of fibrous materials. But Bakelite is strengthened by fibrous materials on account of its low flexibility and other specific properties, probably also by the fact that its fusible parent "A" impregnates homogeneously any fibrous or cellular materials with which it is incorporated, instead of remaining on the surface like rubber or celluloid. It produces, with fibrous fillers, compositions which are strikingly much stronger and less breakable than if it be used alone or in conjunction with structureless fillers. This valuable property has been put to excellent advantage in the manufacture of many moulded and impregnated articles where Bakelite is used in smaller proportions as a binder for fibrous bodies. This is best illustrated by some of the moulded solid buttons, insulators, phonograph records, brush-backs, magneto distributors, knife-handles, pressed plates, and other manufactured objects you see here before you, many of which have been moulded in the hot hydraulic press, without any after-treatment. Some of these articles have been moulded and finished in a few minutes' time; others of large size require some longer heating.

Here is a third rail insulator block, moulded from a mixture of asbestos fibre and Bakelite. From its excellent appearance you would never imagine that it has had two years of strenuous service for heavy passenger traffic on the third rail system of the New York Central lines, exposed to rain and sun and all the extreme conditions of our variable climate.

Moulded compositions of ordinary asbestos and Bakelite, containing less than one-third of Bakelite, have shown on the Riehle testing machine tensile strengths as high as 4490 lbs. per square inch, and by selecting carefully the fibrous material still better results can be obtained.

The following electric tests will give a general idea of the dielectric value of Bakelite and some of its compositions:—

| Composition (a).                                                      | Thickness testing piece in mm. | Volts per mm. at puncture (b). |
|-----------------------------------------------------------------------|--------------------------------|--------------------------------|
| Sample 1 .. .. .                                                      | 1.78                           | 17,400                         |
| Sample 2 .. .. .                                                      | 2.18                           | 14,200                         |
| Sample 3 .. .. .                                                      | 2.60                           | 13,400                         |
| Sample 4 .. .. .                                                      | 0.43                           | 16,750                         |
| Sample 5 .. .. .                                                      | 0.9                            | 23,300                         |
| Sample 6 .. .. .                                                      | 0.95                           | 25,600                         |
| Moulded composition:—                                                 |                                |                                |
| 70 asbestos .. .. .                                                   | 8                              |                                |
| 30 Bakelite .. .. .                                                   | 8                              | 8,500                          |
| Moulded composition, wood flour and Bakelite .. .. .                  | 7.9                            | 11,000                         |
| Impregnated blotting paper, hardened in a hot hydraulic press .. .. . | 3.66                           | 102,000                        |
| Pressed paper impregnated with Bakelite .. .. .                       | 1.6                            | 53,700                         |
|                                                                       |                                | 33,500                         |

(a) Different varieties of transparent "C" made specially for electrical purposes by hardening liquid "A" on a glass plate in a stove.

(b) Tested with a 50 kilowatt transformer, raising voltage gradually so that puncture occurs within twenty to thirty seconds.

Some other tests (Electrical Testing Laboratories of New York) have shown an unusually high specific inductive capacity, which makes the material very suitable for electrical condensers.

Pressed paper, impregnated with Bakelite, has been recommended in Germany for the manufacture of electro

static machines. Its value for this purpose may reside in the fact that it withstands rather well the action of ozone, which is not the case with resins or with hard rubber. In fact, hard rubber is known to coat itself by and by with an extremely thin film of sulphuric acid, due to slow oxidation of the sulphur. This sulphuric layer, although microscopically thin, causes considerable disturbances for some electrical applications. The impregnation of electric coils with Bakelite is now regularly practised on an industrial scale by several electric manufacturing companies. Its advantages for this purpose are obvious on account of the fact that in case of an increase of temperature, through overload or otherwise, the impregnating material cannot melt; but there is another important factor, namely, this substance, notwithstanding its good electric insulating properties, is a better conductor of heat than the resinous materials or varnishes generally used for the impregnation of dynamos or motors, so that the generated heat is better conveyed to the outside. At any rate, it has been observed that coils impregnated with Bakelite heat up much less than others impregnated with resinous bodies.

Bakelite has rendered excellent service as a glue; one of its latest applications on a commercial scale is shown by these brushes, of which the bristles are held together with this binding material, which is indifferent to any of the solvents used in paints, varnishes, paint removers, and to soap or hot water. It is cheaper and easier to apply than rubber, which has lately been used extensively in the United States for the same purpose. Furthermore, the hardening can be conducted at temperatures so low that white bristles are not discoloured.

Let me draw also your attention to these samples of fancy articles, like cigar holders and pipe stems, made of "C," perfectly transparent. Some have the colour of amber; others are as colourless as glass. You will notice that they are entirely devoid of odour or taste, even if you rub them. If I insist on this point it is merely to eliminate an erroneous impression, which has gained some ground, that Bakelite has a particular smell. If there was any smell at all it would only show that the transformation in "C" had not yet been complete.

As chemists you are undoubtedly more interested in the application of Bakelite for laboratory work, or for chemical engineering purposes. Time forbids me to take up the subject in detail. But I may state that a dilute alcoholic solution of "A" finds many uses in the laboratory. Dipping or spraying of metallic objects in or with a solution of the kind, followed by treating in a stove at a temperature of about 120° C. or above, provides them rapidly with a hard protective coating. The time of hardening varies from one minute to half an hour or more, according to the available temperature. If blisters are caused, this indicates that the solution is too thick. This gives us a very economical means for transforming an ordinary sheet-iron kitchen gas-oven, which can be purchased at any hardware store for one to two dollars, into a very efficient substitute for the expensive copper drying stove.

Leaks or cracks in glass apparatus can easily be made tight by the skilful application of this solution. In certain cases asbestos paper or tape, used in conjunction with varnish or Liquid A, will prove an excellent reinforcement.

There is a special variety of Liquid A which can easily be mixed with asbestos fibre, or clay, or silex powder, or baryta, so as to make a very soft dough-like mass.

If I apply this soft mass to a hot steam pipe it will stiffen rapidly until it becomes as hard as stone. By the fact that it contains a base hardening agent, the hardening can take place easily at temperatures as low as 75° C., although higher temperatures will give quicker results. This makes an excellent mixture for spreading on the surface of cast-iron pipes or other parts of machinery which have to be protected against the corrosive action of some chemicals. Here is, for instance, a part of an iron casting, the inside of which has thus been protected by applying this paste as a quarter-inch inside lining. These protected iron castings have been used in a large electrolytic

plant, where they have been submitted for more than a year, day and night, continuously to contact with rapidly moving hot brine and hot chlorine, at temperatures of about 70° C. For such purposes it is always better to apply the material abundantly, because it is very difficult to spread a thin film of any material so uniformly that there should not exist some unprotected places where corrosion can occur.

For certain chemical uses, like digesters, the possibility of chemical corrosion is augmented by mechanical abrasion, due to the friction of moving liquids or solids. For such purposes there exists a simple and efficient way for lining the vessel with acid-proof bricks, held together with Bakelite cement. This is accomplished in a somewhat similar way as porcelain-lined ball mills are made, with that difference that the walls of the vessel ought to be first lined with a thin sheet of asbestos paper, impregnated with liquid A; on this the brick lining is inserted and fastened with liquid A, or better with a cement made with liquid A and some inert filling materials like clay, baryta, or powdered silex, or asbestos. This liquid mixture is easily applied, and then a suitable heater, for instance, a gas-stove, is introduced in the vessel, so as to raise the temperature of the lining to at least 80° C., or higher, until the polymerisation into C has taken place.

Whenever asbestos is used as a filling material, it should not be forgotten that Canadian asbestos is easily attacked by acids. Amphibole asbestos is considerably more resistant to acids; unfortunately, it lacks strength and fibrous qualities. Green Cape asbestos resists acids well, and has a good strong fibre, but is more expensive.

## SOME APPLICATIONS OF WROUGHT TUNGSTEN AND MOLYBDENUM.

By W. D. COOLIDGE.

ONLY a few years ago a number of the elements were classed in the literature as brittle, and had never been produced in a condition in which they were not brittle at room temperature, but have since been taken out of the brittle list. Among these are tungsten and molybdenum.

Prior to their production in ductile form, tungsten and molybdenum as such (that is, other than in alloys or compounds) had but one application, namely, in an incandescent lamp, the one as filament, and the other as filament support.

Some of the physical properties of these last named industrially new elements, together with a rough sketch of the investigation work leading up to the production of ductile tungsten, have been published elsewhere (*Trans. Am. Electrochem. Soc.*, 1910, xvii., 229; *Proc. Am. Inst. E. E.*, 1910, xxix., Part II., 961).

It is the purpose of this paper to tell of some of the applications which are being developed for wrought tungsten and wrought molybdenum. The writer presents it not only for the interest of the work itself, but also in the hope that it will stimulate work on the other so-called brittle metals, and it seems to him that some of our industries are almost certain to profit greatly by the discovery of each new ductile element.

### *The Drawn-wire Tungsten Incandescent Lamp.*

A year and a-half ago the hope was first publicly expressed that it would soon be possible to manufacture lamps on a large scale from ductile tungsten. This hope has been fulfilled, and the commercial development has been so rapid that already the bulk of the tungsten lamps made in this country are of drawn-wire, and the manufacture is already established on a large scale in England and Germany. Some anxiety was at first felt lest it should not be possible to get diamond wire drawing dies of sufficiently small aperture to produce wire fine enough for the



lowest candle-power lamps which might be desired. But this fear proved groundless, and wire is now produced in quantity down to 0.0006 inch in diameter.

Ductile molybdenum is used in some types of lamp as a support material for the tungsten filament.

#### *The Tungsten or Molybdenum-wound Furnace.*

This has already been described by Winne and Dantszen (*Journ. Ind. Eng. Chem.*, 1911, p. 770), and has proved to be an exceedingly useful tool, especially so in connection with the production of wrought tungsten and molybdenum. Extensive factory use has shown it to be not only cheaper, but, regardless of cost, far superior to a platinum-wound electric furnace. When wound on a body of alundum it permits of the attainment of higher temperature than can be reached with platinum. This attainment of the higher temperature is often in itself an advantage, and it is always an advantage, in industrial work, to be relieved from the necessity of using the strictest temperature control to avoid melting a furnace winding. This is especially true in cases where the time consumed in heating up the work in the furnace is important. For in these cases much time is saved by not using a constant current supply to the furnace winding, but by first raising the current, upon the introduction of the cold work, and then bringing it down as the temperature of the work rises.

#### *Electrical Contacts of Tungsten and Molybdenum.*

Tungsten and molybdenum are destined to play a very important rôle in the field of contact-making devices. This is due to their high melting-point, which prevents them from welding together; to their heat conductivity (about twice that of platinum) which tends to keep down local temperature rise, and to their hardness, which enables them to stand repeated impact without flattening out.

The natural assumption would be that both metals under the heat of even minute arcs, which form when the contacts are separated, would oxidise at the points where arcing has taken place, and that non-conducting layers would thus be formed which would produce a high and variable contact resistance. But several things intervene to prevent this. First, there is the relatively good heat conductivity of the dense form of these metals, which distributes the heat. Then the fact that the metals are much less expensive than platinum, for example, makes possible the use of larger contact masses, which again militates against strong local heating. Finally, there is the fact that with both tungsten and molybdenum the oxides which form in the presence of a sufficiently limited amount of oxygen are conducting.

Some promising applications which are being tested out are the following:—

As an iridium substitute in the "master" contacts of Tirrell voltage regulators.

As a silver substitute in the relay contacts of Tirrell voltage regulators.

As an iridium substitute in feed-wire voltage regulators.

As a platinum substitute in railway signal relays.

As a substitute for platinum-iridium in the contacts of a synchronously driven vibrating mechanical rectifier.

As a platinum substitute in telephone jacks.

As a platinum substitute in automobile and stationary gas-engine ignition work, for spark coil contacts, magneto circuit-breaker contacts, and spark plugs.

In connection with the above there was at first serious difficulty in getting satisfactory heat contact between tungsten or molybdenum, on the one hand, and iron or brass, as the case might be, on the other. This was due to the fact that neither tungsten nor molybdenum can be satisfactorily soldered by any of the ordinary processes. This difficulty has been finally entirely overcome.

#### *Tungsten as Target in a Röntgen (X-Ray) Tube.*

This has proved to be, both from the scientific and practical points of view, an exceptionally interesting application.

Until recently platinum has been almost universally regarded as the best target material, and it has so long held undisputed sway in this field that the Röntgen ray worker has come to look upon its limitations as inherent in the Röntgen tube.

It has not been possible until recently to produce dense forged pieces of pure malleable tungsten. But with the advent of this material, the possibilities of the Röntgen tube are greatly extended.

The desiderata in a material to be used as the anti-cathode or target are the following:—

1. High specific gravity.
2. High melting-point.
3. High heat conductivity.
4. Low vapour pressure at high temperature.

The reasons while the above qualities are desirable follow readily from a brief consideration of the theory of Röntgen ray production.

From the concave cathode, electrically charged particles, the electrons are shot out at high velocity in a direction normal to the surface. The paths of these particles converge, and the target is placed at or near the point of strongest convergence, the focus point. When the electron meets an obstruction, as the target, its velocity is reduced, and the denser the target the more rapid is the deceleration. The more rapid the deceleration the greater is the amplitude of the electro-magnetic pulse, the Röntgen ray, sent out. Here, then, is a need for high specific gravity; that of forged tungsten is but little less than that of platinum.

In modern Röntgen ray practice, powerful apparatus running sometimes to a capacity of 6 kilowatts is used to excite the tube. The greater part of the energy delivered to the tube is transformed into heat at the point where the cathode rays bombard the target. Where platinum is used it has been found necessary, to prevent melting, to place the target beyond the focus of the cathode so as to spread the bombardment over a larger area. As a radiograph is a shadow picture, and as the source of the Röntgen ray is the bombarded area of the target, this enlarging of that area is clearly an undesirable thing to do, as the larger area will mean more overlapping and less definition in the resulting picture. In this way the melting-point of platinum has been the limiting feature of the Röntgen tube. The capacity of the tube has been increased by water cooling the platinum, or by using as a target a large mass of copper having a very thin platinum face. But the limit, although raised by this artifice, has still been the melting-point of the platinum.

Tungsten has a much higher melting-point (3000° C. as against 1755° for platinum), and so, even with sharp focussing of the cathode rays on the target, permits the use of more energy than has hitherto been possible; for the high temperature to which it can run enables it to radiate more heat, and its better heat conductivity permits a more rapid flow of heat from the focus spot to the surrounding metal.

Stability of vacuum in a Röntgen tube is of the utmost importance, as the character of the rays is so largely determined by the vacuum. Metal, which under the influence of the high temperature vaporises from the target, condenses on the glass in finely divided form, and absorbs relatively large amounts of gas, thus changing the vacuum. At high temperatures tungsten vaporises least of all the metals.

In the above case, practice seems to be in full accord with the theory, and the tungsten target offers great promise to the Röntgen ray worker. It gives him what he has not had before, an indestructible target, so far as the present electrical apparatus goes, together with sharper definition and much shorter exposure.

#### *Tungsten Projectiles.*

The use of wrought tungsten as a projectile is being carefully investigated. It offers, in this field, possibilities not possessed by any other metal.

The present small arm service projectile is made of lead with a jacket of copper-nickel alloy. The principal advantage of lead over iron, which would of course be cheaper, is that it has a higher specific gravity. Because of this fact a lead bullet will have a smaller cross-section, and will therefore encounter less air resistance to its flight than will an iron bullet of the same weight, and will therefore give a flatter trajectory and longer range. An iron bullet of the same diameter as the lead bullet could, of course, be given the same weight by increasing its length. But this would at once necessitate giving it a higher rotational velocity to keep its axis tangential to its flight. To impart this added rotational velocity calls for the expenditure of energy, and so leaves less for velocity of translation. The lead bullet, then, with its higher density makes possible a flatter trajectory and longer range. With the exception of tungsten, lead is the densest metal which can be considered for this purpose, for gold is the cheapest of the other elements having a higher specific gravity than lead. The density of wrought tungsten is 19.3, while that of lead is 11.5.

For military purposes the softness of lead is not an advantage, a soft nosed bullet being tabooed in civilised warfare. For this reason and because of the fact that it is too weak to hold the rifling, it has to be jacketed with the copper-nickel alloy. To take the rifling and to act as a gas check, the tungsten bullet will require a copper band or its equivalent at the base.

The hardness and high tensile strength of wrought tungsten will give high penetrating power.

The high melting-point of tungsten will prevent it from being harmfully upset at the base by the combined action of the high temperature and rapid impact due to the combustion of the powder charge. (An unsymmetrical upsetting of the base of a projectile is very prejudicial to accuracy).

It would be a very simple matter to calculate the constants of the trajectory of a tungsten projectile were it not for the fact that the high density removes it too far from the present base line. For such calculations one quantity is lacking, the so-called "form factor." This factor could itself be calculated if it contained, as the name would seem to imply, only the dimensions and the specific gravity; but there are also involved in it all of the errors due to simplifying assumptions which have been made in connection with the mathematical derivation of formulae. It therefore becomes necessary to experimentally determine the constants of the trajectory of tungsten bullets, and preparations for this work are now being made.—*Journal of Industrial and Engineering Chemistry*, iv., No. 1.

## THE OIL OF DOUGLAS FIR. A PRELIMINARY STUDY OF ITS COMPOSITION AND PROPERTIES.

By H. K. BENSON and MARC DARRIN.

In the steam distillation of resinous Douglas Fir wood, a crude greenish yellow turpentine of syrupy consistency is obtained. In the distillation process as practised in the Pacific Northwest, steam under a boiler pressure of 45 to 60 abs. is used, and the retorts are usually placed under a diminished pressure at the end of the distillation period for the purpose of removing the last traces of oil from the wood chips.

The yield of this crude turpentine per cord is dependent upon the degree of pitchiness or "fatness" of the wood, but in the case of selected mill waste and stump wood, it ranges from 5 to 7 gallons per cord. When re-distilled under low pressure steam, this yields from 4 to 5 gallons of a water-white turpentine which has a good odour, and complies with the requirements for spirits of turpentine as established by the U.S. Bureau of Chemistry in *Bulletin*

109, revised, Bureau of Chemistry, U.S. Department of Agriculture.

The residue after the removal of the turpentine consists of a clear viscous yellow oil, similar in appearance to the pine oil obtained from the refining of the steam turpentine from Norway, and of Michigan and long leaf pine of the south.

The latter has been studied by Walker (*Massachusetts Institute of Technology Bulletin*, Sept., 1905) and by Teeple (*Journ. Am. Chem. Soc.*, xxx., 412), with conclusions reached in each case that the essential constituent of pine oil is terpineol. Inasmuch as the residual oil from the turpentine distillation of fir wood seemed similar both as to its production and general appearance, and especially since the manufacturers could not dispose of it on account of the oil having to go on the market as fir oil, it seemed desirable to investigate its composition and properties. The present investigation is merely preliminary to a more complete examination of its uses and commercial applications now in progress.

The material consisted of several gallons of the oil from a commercial plant operating in the manner above described. The first effort in studying its properties consisted in a determination of its constants, the following being the mean of a number of determinations:—

### Table of Constants of Fir Oil.

|                                                   |                        |
|---------------------------------------------------|------------------------|
| Colour .. .. .                                    | Light yellow.          |
| Rotation $[\alpha]_D^{20}$ .. .. .                | 37.6° laevo.           |
| Refractivity at 20° C. .. .. .                    | 1.4818.                |
| Solubility in 70 per cent alcohol .. .. .         | 49 oil in 100 alcohol. |
| Acid number .. .. .                               | 1.55.                  |
| Saponification number .. .. .                     | 11.1.                  |
| Iodine number .. .. .                             | 185.0.                 |
| Melting-point (by solid CO <sub>2</sub> ) .. .. . | Below 40° C.           |

The constants for pine oil are described by Teeple (*loc. cit.*), as follows:—

|                                    |                      |
|------------------------------------|----------------------|
| Colour .. .. .                     | Faint yellow colour. |
| Specific gravity .. .. .           | 0.935 to 0.947       |
| Rotation $[\alpha]_D^{20}$ .. .. . | 11° laevo.           |
| Refractivity .. .. .               | 1.4830.              |
| Boiling-point .. .. .              | Begins at 206° C.    |

75 per cent distilling between 211—218°.

Examination was next directed along the line of a possible isolation of its main constituents. For this purpose, 1 litre of fir oil was subjected to repeated fractional distillation and constants determined for each fraction:—

### Constants for Oil of Douglas Fir Fractions.

| Fraction.       | Per cent of total by wt. | Colour.       | Sp. gr. at 20° C. | Lævo rotation $[\alpha]_D^{20}$ | Index refraction 20° C. |
|-----------------|--------------------------|---------------|-------------------|---------------------------------|-------------------------|
| Fir oil .. .. . | —                        | Yellow        | 0.936             | -37.6°                          | 1.4818                  |
| 175—206° C.     | 4.8                      | Yellow        | 0.890             | -42.5                           | 1.4745                  |
| 206—208° C.     | 0.3                      | Yellow        | —                 | —                               | 1.4820                  |
| 208—210° C.     | 0.6                      | Yellow        | —                 | —                               | 1.4750                  |
| 210—212° C.     | 2.2                      | Almost white  | —                 | -40.2                           | 1.4815                  |
| 212—214° C.     | 4.3                      | Almost white  | 0.930             | -40.1                           | 1.4810                  |
| 214—216° C.     | 5.4                      | Almost white  | 0.932             | -40.1                           | 1.4810                  |
| 216—218° C.     | 5.9                      | Almost white  | 0.936             | -40.5                           | 1.4800                  |
| 218—220° C.     | 17.1                     | Almost white  | 0.940             | -43.1                           | 1.4800                  |
| 220—222° C.     | 15.6                     | Yellow        | 0.940             | -45.2                           | 1.4815                  |
| 222—224° C.     | 7.5                      | Yellow        | 0.940             | -46.1                           | 1.4830                  |
| 224—226° C.     | 5.9                      | Yellow        | 0.940             | -46.1                           | 1.4840                  |
| 226—228° C.     | 1.6                      | Yellow        | 0.940             | -44.0                           | 1.4850                  |
| 228—230° C.     | 0.6                      | Yellow        | —                 | —                               | 1.4855                  |
| 230—260° C.     | 2.7                      | Bright yellow | 0.944             | 35.9                            | 1.4880                  |
| Residue .. .. . | 10.0                     | Black         | 0.988             | —                               | —                       |
| Water .. .. .   | 10.0                     | —             | —                 | —                               | —                       |
| Loss .. .. .    | 5.5                      | —             | —                 | —                               | —                       |

### Interpretation of Results of Fractional Distillation.

The boiling-point varies between 175—260° C., 57.4 per cent distilling between 214—226° C., and 33 per cent 218—222° C., yielding products with similar physical con-



stants. This latter fraction represents the chief constituent of fir oil, and to which its properties are mainly due. Further examination of the physical constants shows that the oil is not of a simple nature but represents a mixture of a complex character.

Percentage Composition.

A number of analyses were made of the oil, and the mean results are as follows:—

|                  | Per cent. |
|------------------|-----------|
| Hydrogen .. .. . | 11.9      |
| Carbon .. .. .   | 76.0      |
| Oxygen .. .. .   | 12.1      |
| Nitrogen .. .. . | —         |
| Halogen .. .. .  | —         |
|                  | 100.0     |

*Terpin Hydrate.*—The oxygen content of the oil indicated the presence of an oxygenated terpene, and an attempt was made to ascertain its behaviour toward oxidising agents, such as are used in the preparation of terpin hydrate from terpenes.

1. The fir oil was treated with nitric acid and alcohol in refrigerator. At the end of one week the solution turned deep brown, but no crystals had separated. At the end of one month the solution had turned black, and formed a very viscous-like tar, and possessed a very strong camphor odour. Well formed colourless crystals of the hydrate had formed, m. p. 117° C. Yield of terpin hydrate, 13 per cent of fir oil. The remaining oil was subjected to a continued steam distillation, and yielded a small amount of a clear slightly yellow oil with a camphor-like odour. This was probably due to an oxidation product of the oil by the nitric acid.

2. Fir oil was hydrolysed with 5 per cent sulphuric acid at ordinary temperature. At the end of a week the oil layer was filled with a multitude of clear radiating needle-like crystals. These crystals kept slowly growing until, at the end of the second week, they covered the bottom of the dish. M. p. of crystals, 117–118° C.

*Test for Ketones.*—Separate samples of fir oil were treated with saturated solutions of (a) sodium bisulphite and (b) ammonia, for a period of one month. In neither case were there indications of crystalline derivations—tending to show the oxygen found by analysis was not of an aldehydic or ketonic nature.

From a study of the above data the authors conclude that fir oil owes its properties to the presence of terpineol. This conclusion is based on a number of considerations. The double ethylene bond readily accounts for the high iodine absorption. The agreement of the percentage composition with terpineol (H, 11.7; C, 78.0; O, 10.3) is strikingly close when the presence of other constituents is considered. The ease by which terpin hydrate is formed from fir oil by the action of dilute sulphuric acid strongly indicated terpineol, since the latter is an intermediate product in the formation of a terpin from a terpene. The constants for terpineol are as follows:—

|                                 |                 |
|---------------------------------|-----------------|
| Boiling-point at 760 mm. ..     | 217–218° C. (a) |
| Specific gravity at 15° .. ..   | 0.935–0.940 (a) |
| Refractivity $n_D^{20}$ .. .. . | 1.48084 (a)     |
| Melting-point .. .. .           | 35° (b)         |

(a) Gildermeister and Hoffman, p. 140.

(b) *Liebig's Ann.*, cclxxv., 104.

The close agreement of the fir oil and especially of the fractions between 218–220° is very marked with the exception of the melting-point, the fir oil solidifying below –40° C. and the fractions between 218–220° at 0° C. This exception is not unusual in the presence of impurities, as it has been shown by Bouchardat and Voiry (*Comptes Rendus*, civ., 996; *Ber.*, xx., 286) that terpineol, which will not solidify above –50° C., has a melting-point of 30–32° C.

The conclusion drawn from these tests is that not less than one-third of fir oil consists of terpineol, and that fir oil is so closely similar to pine oil in its properties as to be able to be substituted for the latter in its commercial application.

The uses of the latter have become very extensive in the last few years. As a solvent for varnish gums in the cold, for rubber, for nitrocellulose lacquer, in the manufacture of metal polishes, and for general use as an essential oil, it is being sold regularly in carload lots. This same market should be open in the future to fir oil for the same or similar uses.—*Journal of Industrial and Engineering Chemistry*, iii., No. 11.

A NOTE ON THE ASSAY OF FORMALDEHYDE.\*

By ELIAS ELVOVE.

It has been shown by Williams (*Journ. Am. Chem. Soc.*, 1905, xxvii., 596) that the two different types of methods for estimating formaldehyde, namely, those dependent on the oxidation of the formaldehyde and those dependent on its forming condensation products, do not yield concordant results. In explanation of this discrepancy, Williams advances the view "that either the condensation reactions are not complete or a small part of the formic acid is oxidised further." He also reaches the conclusion that the hydrogen peroxide method is the most satisfactory for strong impure solutions; while "the potassium cyanide method is recommended for dilute impure solutions." Recently, the writer has had occasion, in connection with the study of embalming fluids which has been in progress in the Hygienic Laboratory, U.S. Public Health and Marine Hospital Service, Washington, D.C., to make a comparatively large number of determinations of the quantity of free formaldehyde in these fluids. (It is expected that the results of this study will shortly be published as a Hygienic Laboratory Bulletin.) Owing to the possible presence in such fluids of substances other than formaldehyde which on oxidation will yield acids (thus rendering the hydrogen peroxide method inapplicable), or other reducing substances (thus invalidating the iodometric method), it was found necessary to resort to one of the condensation methods, and the potassium cyanide method was chosen. It became of interest therefore to look into the points raised by Williams as to the discrepancy of the results obtained by the oxidation and condensation methods, and the possible incompleteness of the condensation reactions.

The methods investigated by Williams were those which are most generally recommended for the determination of formaldehyde, namely, the ammonia method of Legler (*Ber.*, 1883, xvi., 1333), the hydrogen peroxide method of Blank and Finkenbeiner (*Ber.*, 1898, xxxi., 2979), and the iodometric and potassium cyanide methods of Romijn (*Zeit. Anal. Chem.*, 1897, xxxvi., 18). His conclusion that the results obtained by the condensation methods are lower than those obtained by the oxidation methods, is in harmony with the previous work of Smith (*Journ. Am. Chem. Soc.*, 1903, xxv., 1028), who also found that, as compared with the Legler method, "the hydrogen peroxide method almost invariably gave higher results." Smith also seems to hold the view that the potassium cyanide method is applicable to dilute solutions only, since he refers to the KCN method as a "method which is applicable to solutions containing but small quantities of formaldehyde"; and while he concludes that "the iodometric and potassium cyanide methods give good results on dilute solutions," he adds that "it should be remembered that in diluting strong solutions to the range of these methods, a small error in weighing may be considerably multiplied." Apparently influenced by this suggestion of Smith, many authors on analytical chemistry do not recommend the

\* *The Chemical Engineer*, xiv., No. 6.

potassium cyanide method except in the case of dilute solutions. Thus Leffmann and Beam ("Food Analysis," 1905, 2nd ed., p. 84), referring to the work of Smith, state that for the determination of formaldehyde the choice of the method "will depend on the strength of the solution," recommending the iodine method of Romijn in the case of moderately strong solutions and the potassium cyanide method for dilute solutions. Likewise, from Schimpf ("Manual of Volumetric Analysis," 1909, 2nd ed., p. 644), who also refers to the work of Smith, one gains the information that "the Blank and Finkenbeiner method is very satisfactory for strong solutions" and the "iodometric and potassium cyanide methods give good results on dilute solutions." Similarly, Leach ("Food Inspection and Analysis," 1907, 2nd ed., p. 819), omits the potassium cyanide method as a suitable method for determining formaldehyde in the commercial preservative, although listing the iodometric method (see Note a), the method of Blank and Finkenbeiner and the ammonia method; while the potassium cyanide method he recommends only in the case of very dilute solutions such as are met with when determining formaldehyde in milk (see Note b). The impression therefore which one obtains from the literature on the subject as has been referred to, is that while the potassium cyanide method is admittedly a very good method for determining formaldehyde in dilute solutions, it is not recommended in the case of the concentrated or moderately strong solutions, and that in such cases it is preferable to use one of the other methods, of which the hydrogen peroxide method is the most favoured. An examination of the leading pharmacopœias as to the methods chosen for assaying commercial formaldehyde solutions also seems to confirm the conclusion that the potassium cyanide method is not generally regarded as a method suitable for use in such cases. Thus the U.S. Pharmacopœia (1905) adopts the hydrogen peroxide method, the German Pharmacopœia (1910) gives the acidimetric sodium sulphite method, the British Pharmaceutical Codex (1907) recommends the ammonium chloride and iodometric methods, while the French Pharmacopœia (1908) agrees with the U.S. Pharmacopœia in giving preference to the hydrogen peroxide method. Finally, we may mention that according to Fresenius and Grünhut (see Note c) there really are only four methods in use for assaying commercial formaldehyde, namely, the ammonia method of Legler, the method in which the formaldehyde is treated with sodium hydroxide in pressure bottles, the hydrogen peroxide method of Blank and Finkenbeiner, and the iodometric method of Romijn.

(NOTE a. "Food Inspection and Analysis," 1907, 2nd ed. p. 819. It may be noted in this connection that both here and in the first edition, p. 665, there seems to be an error in some of the figures given. For if we take 10 cc. of a 3 per cent formaldehyde solution—it is directed that the solution is to be diluted "to a strength not exceeding 3 per cent"—we will be operating on about 0.3 gm.; and since "two atoms of iodine are equivalent to one molecule of formaldehyde," 0.3 gm. HCHO will require 200 cc. of N/10 iodine, whereas according to the given directions only 25 cc. of N/10 iodine are to be taken. The same error is found also in Leffmann and Beam, "Food Analysis," 1905, 2nd ed., p. 84).

(NOTE b. "Food Inspection and Analysis," 1907, 2nd ed., p. 181. There seems to be also an oversight in this connection, since it is directed to use ferric chloride as the indicator in titrating the excess of silver.

(NOTE c. *Zeit. Anal. Chem.*, 1905, xlv., 13. "Doch sind es—soweit unsere Kenntnis reicht—im wesentlichen nur vier Verfahren, deren man sich in der Technik zur Betriebskontrolle, sowie zur Wertbestimmung des Handelsproduktes, bedient: die Ammoniak-Methode von Legler, die Oxydation mit Natronlauge in Druckflaschen, die Wasserstoffsperoxyd-Methode von Blank und Finkenbeiner, und endlich die jodometrische Methode von Romijn").

On the other hand, the meaning of the objection advanced by Smith against the use of the potassium cyanide method for determining formaldehyde in strong solutions, namely, "that in diluting strong solutions to the range of these methods, a small error in weighing may be considerably multiplied," is difficult to understand. For supposing that 1 gm. of the formaldehyde solution is weighed out, diluted with distilled water to 100 cc., and 25 cc. of the resulting solution taken for the analysis, and supposing that the delicacy of the balance used is only  $\pm 0.001$  gm., then the actual amount taken for the analysis would be  $0.250$  gm.  $\pm 0.00025$  gm., involving therefore a possible error of  $\pm 0.1$  per cent. Now, if the step of diluting and taking for the analysis an aliquot portion were omitted and the total amount weighed out were used for the analysis, the amount so taken would be  $1.0 \pm 0.001$  gm.; the possible error involved would therefore be exactly the same as before, namely,  $\pm 0.1$  per cent. It is possible that "error in weighing" is an oversight, the intention having been—error in measuring. If this was the intention, we can readily see how an error might be introduced through an error in measuring. For supposing that instead of using for the analysis the entire amount weighed out, it be diluted to a definite volume and 5 cc. of this solution taken for the analysis. In measuring out the 5 cc. there might be an error, say, of  $\pm 0.05$  cc. This would introduce an error of  $\pm 1$  per cent, which would have been avoided if the analysis had been carried out directly on the weighed amount of formaldehyde solution. But even in this case the error would not be "multiplied," unless more than one dilution be made. Moreover, if instead of using only 5 cc. of the diluted solution a larger volume be taken, say, 25 cc., an equal absolute error in the measuring would, of course, relatively be only one-fifth, or reducing the possible error from  $\pm 1$  to  $\pm 0.2$  per cent. In other words, a procedure which would involve the dilution of a certain weight of the strong formaldehyde solution to 100 cc. and the use of 25 cc. of the diluted solution for the analysis, would ordinarily involve no greater error than the inherent errors of volumetric analysis. And since all the methods compared are volumetric, any such errors may be considered equally possible in all of them. For supposing that in measuring out the 25 cc. of the diluted formaldehyde solution there might be an error of  $\pm 0.05$  cc. or  $\pm 0.2$  per cent, might there not also be a similar error when the same measuring instrument will be used for measuring out the 25 cc. of twice normal NaOH (according to Smith) in the case of the hydrogen peroxide method? Besides, in taking 25 cc. of the 100 cc. of the diluted formaldehyde solution it is not necessary that the measuring instrument used should measure out exactly 25 cc., but only that the volume so measured out be one-fourth of the total, and whether this is the case can be readily and conveniently ascertained by using the same measuring instrument for filling the empty 100 cc. flask with water and seeing whether four fillings will fill it exactly to the mark. This will prove the accuracy of the instrument for this purpose, or enable the operator to apply the proper correction. It would seem therefore that if the potassium cyanide method is an excellent method for determining formaldehyde in dilute solutions it may be used with equal advantage in the case of strong solutions by suitably diluting the latter with water.

That such is really the case may be seen from Smith's own results. Using the potassium cyanide method for strong formaldehyde solutions, in which case "all solutions containing more than 1 per cent were diluted," the three results given in the case of the 37 per cent formaldehyde solution are:—37.12, 37.07, and 37.18 per cent. Likewise, the results of Williams, when using the potassium cyanide method for determining the formaldehyde in the concentrated solution, show that very concordant results are obtained by this method. Thus, six determinations yielded the following percentages:—35.15, 35.06, 35.23, 35.01, 35.21, 35.07, or a maximum difference from the average (35.12) of only 0.11 per cent. When using the

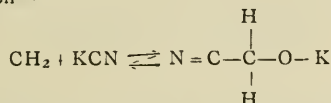


hydrogen peroxide method, four determinations yielded the following percentages:—35·82, 35·92, 35·74, and 35·78, or a maximum difference from the average (35·81) of 0·11 per cent. It is thus seen that the potassium cyanide method can be applied to strong formaldehyde solutions by suitably diluting them, the results thus obtained being equally concordant as those obtained by the hydrogen peroxide method. It therefore remains only to clear up the point as to whether or not the lower results obtained by the potassium cyanide method as compared with those obtained by the hydrogen peroxide method may be due to possible incompleteness of the reaction between the KCN and the formaldehyde.

If we will suppose that the reaction between the KCN and the formaldehyde is not complete, we must assume that the value of  $c_1 p_1 q_1$  in the general equation—

$$V = v - v_1 - c p q - c_1 p_1 q_1,$$

which is the fundamental equation underlying all chemical dynamics (Jones, "Elements of Physical Chemistry," 1907, 3rd ed., p. 529), is not negligible but has a value which would account for the lower results obtained by the KCN method. That is, in the reaction between the formaldehyde and the KCN, which may be represented by the equation—



we must assume that the velocity of the reaction which tends to decompose the condensation product back into formaldehyde and KCN has an appreciable value. From the law of mass action it would follow therefore that if we were to vary the mass of one of the reacting substances the point at which equilibrium is established should also vary; just as in the classical instance of an incomplete reaction, namely, the reaction between acetic acid and ethyl alcohol, in which case Berthelot and Pean de Saint Gilles ("Elements of Physical Chemistry," 1907, 3rd ed., p. 522) found that by varying the amount of alcohol with respect to that of the acid the amount of ester produced also varied, being only 66·5 per cent of the theory when one equivalent of alcohol was used, but increasing to 82·8 per cent when two equivalents of the alcohol were added. In order therefore to determine whether any such variation occurs in the case of the reaction between formaldehyde and KCN, the following experiments were carried out on mixtures of formaldehyde and KCN, in which the amount of KCN added varied from approximately one to three equivalents.

#### Mode of Procedure.

A formaldehyde solution was prepared by diluting 21·1879 grms. of a sample of U.S.P. solution of formaldehyde to 2000 cc. with distilled water. Portions of 15 cc. of this solution were mixed at room temperature (22–25° C.) with varying amounts of approximately N/10 KCN, the minimum amount of which was just a little in excess of that theoretically required to combine with all of the formaldehyde taken, while the maximum amount of KCN used was about two equivalents more than necessary for a complete equimolecular union. The KCN solution was prepared from a sample of Kahlbaum's potassium cyanide, and its value in terms of tenth-normal silver nitrate was determined simultaneously with each series of experiments, the determination being carried out in a manner similar to that used for determining the uncombined cyanide in the experiments. The mixing of the formaldehyde and potassium cyanide solutions was generally effected in Erlenmeyer flasks, and immediately after mixing (the latter operation consuming about half a minute), the resulting solution was added to a mixture of a known amount of silver nitrate and nitric acid in a 200 cc. measuring flask. The amount of silver nitrate used was

sufficient in every case to combine with all of the excess of KCN, and calculated to leave in the filtrate, for the subsequent titration, the equivalent of about 2 cc. of N/10 KCNS per 100 cc. of the filtrate. The amount of nitric acid used was 10 or 20 cc. of U.S.P. dilute (10 per cent) nitric acid. After thoroughly washing the Erlenmeyer flask in which the KCN and formaldehyde solutions were mixed and adding the washings to the flask containing the acidified silver nitrate solution, the whole was made up to 200 cc. with distilled water, thoroughly shaken, filtered through a dry filter, and 100 cc. of the filtrate titrated for the excess of silver by means of N/10 KCNS, using 2 cc. of a 10 per cent ferric alum solution as indicator. The results obtained are given in Table I.

TABLE I.—Effect of Varying the Excess of KCN.

| No. of experiment. | Amount of formaldehyde solution taken. | Amount of N/10 KCN added. (a) | Amount of N/10 AgNO <sub>3</sub> used. | N/10 KCNS required for one-half of filtrate. | Found equivalent of the formaldehyde solution in terms of N/10 AgNO <sub>3</sub> . |
|--------------------|----------------------------------------|-------------------------------|----------------------------------------|----------------------------------------------|------------------------------------------------------------------------------------|
|                    | Cc.                                    | Cc.                           | Cc.                                    | Cc.                                          | Cc.                                                                                |
| 1                  | 15                                     | 19·7                          | 4                                      | 1·50                                         | 18·45                                                                              |
| 2                  | 15                                     | 20·0                          | 4                                      | 1·45                                         | 18·65                                                                              |
| 3                  | 15                                     | 21·0                          | 5                                      | 1·55                                         | 18·84                                                                              |
| 4                  | 15                                     | 22·0                          | 6                                      | 1·67                                         | 19·07                                                                              |
| 5                  | 15                                     | 23·0                          | 7                                      | 1·75                                         | 19·21                                                                              |
| 6                  | 15                                     | 24·0                          | 8                                      | 1·75                                         | 19·20                                                                              |
| 7                  | 15                                     | 25·0                          | 9                                      | 1·80                                         | 19·29                                                                              |
| 8                  | 15                                     | 27·0                          | 11                                     | 1·85                                         | 19·36                                                                              |
| 9                  | 15                                     | 30·0                          | 14                                     | 1·83                                         | 19·29                                                                              |
| 10                 | 15                                     | 40·0                          | 24                                     | 1·90                                         | 19·30                                                                              |
| 11                 | 15                                     | 50·0                          | 34                                     | 1·98                                         | 19·34                                                                              |
| 12                 | 15                                     | 60·0                          | 44                                     | 2·02                                         | 19·29                                                                              |

(a) The KCN solution was only approximately tenth normal, 48 cc. being equivalent to 47·4 cc. N/10 AgNO<sub>3</sub>.

The results given in Table I. show that the maximum result was reached when the excess of KCN was about one-half of an equivalent (Exp. 8), while further increasing the amount of KCN up to approximately three equivalents did not appreciably alter the result. The reaction may therefore be regarded as complete, at least for all practical purposes, when the excess of KCN is as much as one-half of an equivalent. On the other hand, when the excess of KCN is less than one-fourth of an equivalent (Exps. 1–6), the reaction is incomplete; and when the amount of KCN added is only slightly in excess of that required to combine with all of the formaldehyde present, the result is about 3 or 4 per cent too low (Exps. 1–2). That the excess of KCN must be above a certain minimum in order to ensure a complete reaction is not brought out either in the original paper of Romijn or those of Smith or Williams. In fact, none of the literature examined has any reference to this point; while from the statement of Romijn that the method is based on the property of formaldehyde to *immediately* add itself to potassium cyanide ("die Eigenschaft des Formaldehyds, das Cyankalium sofort zu addiren," *Zeit. Anal. Chem.*, 1897, xxxvi., 18), and his unmodified general statement that when the KCN is in excess so much of the KCN becomes combined as to correspond to one molecule of KCN for every molecule of formaldehyde ("weil ein Ueberschuss von Cyankalium vorhanden war, wird von dem Cyankalium so viel gebunden, das auf ein Molekül Formaldehyd ein Molekül Cyankalium kommt," *Ibid.*), one might suppose that the relative amount of the excess of KCN to be added does not matter. This conclusion would gain further support from the statement of Smith (*Journ. Am. Chem. Soc.*, 1903, xxv., 1032) that the determination is carried out by mixing the formaldehyde "with a known quantity of potassium cyanide," the latter being in excess.

In order to determine the effect of varying the time or the temperature, two series of experiments were carried out. In one of these, the mixtures of formaldehyde and

KCN were allowed to stand for different intervals of time at the constant temperature of  $15^{\circ}\text{C}$ ., and the residual cyanide then determined in the usual way. In the other, the time was constant, but the temperature was made to vary between  $5^{\circ}\text{C}$ . and  $40^{\circ}\text{C}$ . In those cases, where the mixtures had to stand for a considerable length of time, the flasks containing same were tightly stoppered by means of glass or rubber stoppers, and the value of the KCN solution was controlled by letting it stand under similar conditions and determining its strength at the end of the experiment. The experiments designed to show the effect of temperature were carried out as follows:—The formaldehyde solution was placed in one Erlenmeyer flask while the KCN solution which was to be added to it was placed in another similar flask, and both were then warmed or cooled to the desired temperature by being set in a large water-bath which was kept about a degree above or below the desired temperature respectively. The time thus consumed was about half an-hour. The KCN solution was then poured into the flask containing the formaldehyde solution, and the mixture quickly transferred back again into the flask which contained the KCN solution, and mixed in the usual way, while the flask containing the solutions was still immersed in the water-bath. This mixture was then quickly poured into a mixture of silver nitrate and nitric acid, in a 200 cc. measuring flask, and mixed with it. (The amount of  $\text{AgNO}_3$  varied as shown in the tables, while the amount of  $\text{HNO}_3$  was the same in all cases, namely, 20 cc. of 10 per cent nitric acid). Both flasks were then thoroughly washed with distilled water, the washings added to the silver solution, and the whole made up to 200 cc. From this point the procedure was the same as that already described. Each of the different conditions of time and temperature was studied with three different KCN excesses, namely, a KCN excess of approximately one-hundredth, one-fourth, and one-half of an equivalent respectively. The results obtained are given in Tables II. and III.

TABLE II.—Effect of Varying the Time.  
(Temperature,  $15^{\circ}\text{C}$ .)

| No. of experiment. | Time mixture stood before added to silver solution. | Amount of formaldehyde solution taken. | Amount of KCN added (a). | Amount of N/10 $\text{AgNO}_3$ used. | N/10 KCN required for one-half of filtrate. | Found equivalent of the formaldehyde solution in terms of N/10 $\text{AgNO}_3$ . |
|--------------------|-----------------------------------------------------|----------------------------------------|--------------------------|--------------------------------------|---------------------------------------------|----------------------------------------------------------------------------------|
|                    |                                                     | Cc.                                    | Cc.                      | Cc.                                  | Cc.                                         | Cc.                                                                              |
| 1                  | 0 (b)                                               | 25                                     | 33                       | 5                                    | 1'80                                        | 31'33                                                                            |
| 2                  | 0 (b)                                               | 25                                     | 40                       | 12                                   | 2'30                                        | 32'27                                                                            |
| 3                  | 0 (b)                                               | 25                                     | 48                       | 20                                   | 2'38                                        | 32'36                                                                            |
| 4                  | 1                                                   | 25                                     | 33                       | 5                                    | 1'80                                        | 31'33                                                                            |
| 5                  | 1                                                   | 25                                     | 40                       | 12                                   | 2'30                                        | 32'27                                                                            |
| 6                  | 1                                                   | 25                                     | 48                       | 20                                   | 2'40                                        | 32'40                                                                            |
| 7                  | 18                                                  | 25                                     | 33                       | 5                                    | 1'82                                        | 31'37                                                                            |
| 8                  | 18                                                  | 25                                     | 40                       | 12                                   | 2'25                                        | 32'17                                                                            |
| 9                  | 18                                                  | 25                                     | 48                       | 20                                   | 2'35                                        | 32'30                                                                            |
| 10                 | 42                                                  | 25                                     | 33                       | 5                                    | 1'85                                        | 31'43                                                                            |
| 11                 | 42                                                  | 25                                     | 40                       | 12                                   | 2'30                                        | 32'27                                                                            |
| 12                 | 42                                                  | 25                                     | 48                       | 20                                   | 2'35                                        | 32'30                                                                            |

(a) Added immediately after mixing.

(b) 48 cc. of the KCN solution was equivalent to 47'56 cc. N/10  $\text{AgNO}_3$ .

From the results given in Table II. it is seen that when the mixture of KCN and formaldehyde is allowed to stand forty-two hours, the result obtained is practically the same as when the mixture is immediately added to the silver solution. From the results given in Table III. it is seen, however, that a variation in the temperature does have an appreciable effect on the results obtained, especially when the KCN added is only slightly in excess of that required to combine with all of the formaldehyde present. That this is so may also be seen from the following experiments:—To each of four Erlenmeyer flasks there were added 25 cc. of a dilute formaldehyde solution and 33 cc. of an approximately N/10 KCN solution, and the flasks tightly

stoppered by means of rubber stoppers. From the known value of the formaldehyde and KCN solutions the amount of KCN added was calculated to be approximately one-hundredth of an equivalent in excess of that required to combine with all of the formaldehyde present. All these flasks were then set in a large water-bath, the temperature of which was kept at about  $40^{\circ}\text{C}$ ., and allowed to remain in this bath for half-an-hour. At the end of this time, the contents of flask No. 1 was added to a mixture of 5 cc. N/10  $\text{AgNO}_3$  and 20 cc. of 10 per cent nitric acid in a 200 cc. measuring flask, and the analysis completed as in the former experiments; while flasks Nos. 2, 3, and 4 were taken out of this bath and set in another large water-bath, which was kept at about  $5^{\circ}\text{C}$ . After remaining in this bath for half-an-hour, No. 2 was treated as No. 1, while Nos. 3 and 4 were taken out and placed again in the bath at  $40^{\circ}\text{C}$ . After this second warming to  $40^{\circ}\text{C}$ ., No. 3 was treated as were Nos. 1 and 2, while No. 4 was taken out of this bath and set again in the bath at  $5^{\circ}\text{C}$ . After this second cooling to  $5^{\circ}\text{C}$ ., No. 4 was treated as those preceding it. On titrating half of the final filtrate with N/10 KCNS, the results shown in Table II. were obtained.

(To be continued).

## NOTICES OF BOOKS.

*A Dictionary of Applied Chemistry.* By Sir EDWARD THORPE, C.B., LL.D., F.R.S. Vol. I. Revised and Enlarged Edition. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1912. (£2 5s. net).

THE revised and enlarged edition of Sir Edward Thorpe's Dictionary of Applied Chemistry, of which this is the first volume, is to be issued in five volumes, and it is hoped that the entire work will be published within two years. The alphabetical arrangement of the earlier edition is preserved, and vol. i. covers A to CHE. It has been so thoroughly revised and brought up to date that it may be regarded as practically a new work which has been prepared with the utmost care, and with the aid of the most eminent authorities in the scientific world. The new edition of the Dictionary will no doubt stand the test of time as well as the old, and will be as valuable and as much used a volume in the libraries of colleges and technical schools.

*An Elementary Text-book of Metallurgy.* By A. HUMBOLDT SEXTON, F.I.C., F.C.S. Fifth Edition. London: Charles Griffin and Co., Ltd. 1911. (6s.).

THIS elementary treatise on metallurgy is too well known to need recommendation. As a first text-book it is unsurpassed, and students who make use of it find that it gives them a thoroughly satisfactory foundation for their more advanced work in the subject. A short course of practical work is included in it. The fifth edition, which has appeared very shortly after the fourth, contains but few alterations, and those are of comparatively trifling importance.

*A First Year Physical Chemistry.* By T. P. HILDITCH, D.Sc. (Lond.), F.I.C. London: Methuen and Co., Ltd. 1912. (2s.).

THIS book could very well be used after or in conjunction with an intermediate course of inorganic and organic chemistry, and as an introduction to the study of physical chemistry. The author lays considerable stress on the historical aspects of physical chemistry, and as far as possible connects all facts and theories with the great names of the science. His explanations are brief and to the point, and he shows good judgment in not overburdening the text with details; the treatment is very



systematic, and the amount of mathematics introduced is reduced to the minimum. The author is obviously well acquainted with the difficulties and slight obscurities which often retard the progress of the student at the beginning of his course. The applications of physical chemistry are well treated in the last part of the book, and an outline of suitable practical work is added, while the glossary of terms used in the science and of the most important formulæ will be found very useful for revision purposes. The book should be widely used in technical schools; it gives unprecedented value for its extremely moderate price.

*Physico-chemical Calculations.* By JOSEPH KNOX, D.Sc. London: Methuen and Co., Ltd. 1912. (2s. 6d.).

STUDENTS who are attending an elementary course of physical chemistry, and are doing some practical work in the subject, will find this book very useful. It is based upon a similar work written in German, "Physikalisch-chemische Rechenaufgaben," by Abegg and Sackur, but differs from it in a good many respects. The problems have been re-arranged and many solved problems have been added, while short explanations of the theory involved in the problems are given as introductions to each chapter. All the chief sub-divisions of physical chemistry are taken into consideration, and the problems have been in the main taken direct from the original literature. They are of a very diversified type, and differ greatly in difficulty. None of them, however, should be beyond the powers of the student who is possessed of a fair equipment of mathematical knowledge, and they have been carefully chosen as typical examples. Answers are provided to all the problems given for solution.

*Church's Laboratory Guide.* Revised and largely Rewritten by EDWARD KINCH, F.I.C., &c. Ninth Edition. London: Gurney and Jackson. Edinburgh: Oliver and Boyd. 1912. (6s. 6d. net).

THIS laboratory guide has been used in many agricultural colleges and technical schools, and has also been found very useful by analysts who have had to analyse agricultural materials and products. It contains a preliminary course in which methods of manipulation, the preparation of various elements and compounds, and the investigation of common substances of agricultural interest are described. A full scheme of qualitative analysis is given in the second part, and quantitative analysis is treated in Part III. Special attention is paid to the analysis of soils, manures, feeding-stuffs, and dairy produce, and some new processes have been included for the first time in the ninth edition.

*Soap Bubbles.* By C. V. BOYS, F.R.S. New and Enlarged Edition. London: Society for Promoting Christian Knowledge. 1912.

THE first edition of this book had such a wide circulation that the author was encouraged to issue it in an enlarged and somewhat altered form. Addressed to young people, it tells in simple and interesting language of the forces which mould soap bubbles, discusses the colours of bubbles, and explains the meaning of capillarity and of the laws governing the formation of soap films and liquid drops. Many simple experiments are described, and the illustrations make it very clear how they are to be performed. The author devotes a chapter to practical hints relating to the preparation of the bubbles and the methods of carrying out some of the experiments, and he goes so fully into details that there should be no difficulty in getting satisfactory results. The book will no doubt inspire the young student to try many of the experiments for himself and perhaps to devise others, and the treatment of the theoretical side of the subject is so clear that quite a good knowledge of the elementary statics of liquids could be gained from it.

*A School Chemistry.* By F. R. L. WILSON, M.A., and G. W. HEDLEY, M.A. Oxford: The Clarendon Press. London, Edinburgh, New York, Toronto, and Melbourne: Henry Frowde. 1912. (4s. 6d.).

THIS book, which contains lessons in both practical work and theory, is a shorter course than that given in the Elementary Chemistry by the same authors, and presents the same excellent features as that work. The authors put before the young student a particularly high ideal as regards their written descriptions of their work, and a boy who has worked through the course will have received a thorough training not only in the manipulation of apparatus and in making the fullest use of his powers of observation, but also in the recording of his results in a clear, direct style. Many recent examination papers have been added, and throughout the book very good sets of questions are given, besides practical problems for exercising the skill and ingenuity of the quicker students.

*Kelly's Directory of Chemists and Druggists* (1912) in England, Scotland, and Wales, and the principal Towns in Ireland, Channel Islands, and Isle of Man. London: Kelly's Directories, Ltd. (20s.).

THE work is much more comprehensive than the title implies, as it contains in addition to the chemists and druggists and drug stores the names and addresses of the manufacturing chemists, wholesale druggists, drysalers, dentists, veterinary surgeons, hospitals, surgical instrument makers, photographers, photographic material makers and dealers, and all other trades connected therewith. Some interesting statistics are given in the preface, from which it appears that in 1906, the date when the last edition was published, the exports of produce and manufactures of chemicals and chemical preparations amounted to £7,907,173 as against £9,007,060 in the year 1910, showing a very substantial increase.

## CORRESPONDENCE.

### ALCHEMY.

*To the Editor of the Chemical News.*

SIR,—Those of your readers interested in the early history of chemistry may like to know that on Friday, May 10th, at 7.30 p.m., I hope to deliver a public lecture dealing with the origin and development of Alchemy. For this purpose I have engaged the Green Salon of Eustace Miles Restaurant, Chandos Street, Charing Cross, W.C. There will be no charge for admission to this lecture.

Thanking you in anticipation for affording this letter the hospitality of your columns,—I am, &c.,

H. STANLEY REDGROVE,

(Author of "Alchemy: Ancient and Modern," &c.).

The Polytechnic, Regent Street, W.,  
April 20, 1912.

Royal Institution.—On Tuesday, April 30th, at 3 o'clock, Mr. F. Balfour Browne begins a course of two lectures at the Royal Institution on "Insect Distribution, with special reference to the British Islands"; on Thursday, May 2nd, Prof. J. Norman Collie gives the first of two lectures on "Recent Explorations in the Canadian Rocky Mountains"; and on Saturday, May 11th, Mr. H. Plunket Greene begins his course of three lectures on "Interpretation in Song," with vocal illustrations; Mr. S. Liddle will be the accompanist. The Friday Evening Discourse on May 3rd will be delivered by Mr. W. C. Dampier Whetham on "The Use of Pedigrees"; and on May 10th, by Prof. W. Stirling, on "The Gaumont Speaking Cinematograph Films" (illustrated by the aid of Mons. Gaumont).

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. cliv., No. 8, February 19, 1912.

**Compounds of Neodymium.**—Paul Joye and Charles Garnier.—By spectroscopic methods the authors have discovered the existence of three different varieties of neodymium hydrate. When the hydrate is precipitated in the usual way it gives in reflected light a well-defined absorption spectrum. After it has been heated to 1000° it gives a reflection spectrum which has already been described as belonging to the oxide  $\text{Nd}_2\text{O}_3$ . The light reflected by the hydrate which has been heated to various temperatures between 300° and 700° gives two different spectra, quite unlike those of the hydrate and oxide. The author's experiments demonstrate the existence of a second hydrate,  $2\text{Nd}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ , formed from  $\text{Nd}_2\text{O}_3 \cdot 6\text{H}_2\text{O}$  by the loss of 3 molecules of water.

**s-Dioxy-thionaphthene.**—Maurice Lanfry.—The author proposes to call those thiophenic molecules in which the oxygen is fixed to the sulphur s-oxy derivatives. He has prepared an s-dioxy-thionaphthene by the action of hydrogen peroxide on thionaphthene in dilute boiling acetic solution. It does not possess the properties of the phenols, nor ketones, nor quinones. When treated with excess of bromine it gives a dibromide,  $\text{C}_8\text{H}_6\text{SO}_2\text{Br}_2$ . Apparently the fixation of oxygen by the sulphur of thiophenic hydrocarbons greatly facilitates the formation of bromine addition products. Fuming nitric acid instantly dissolves s-dioxy-thionaphthene, and from the solution crystals of the mononitro compound separate out.

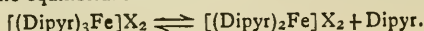
**Action of Bromine in Presence of Aluminium Bromide on Methylcyclohexanols.**—F. Bodroux and F. Taboury.—The bromination of the three methylcyclohexanols by bromine in presence of aluminium bromide gives results analogous to those obtained with cyclohexanol. The action is energetic and yields a solid product and a yellowish oil. The former consists almost entirely of pentabromotoluene, while the oil is a mixture of several brominated derivatives.

*Berichte der Deutschen Chemischen Gesellschaft,*  
Vol. xlv., No. 3, 1912.

**Use of Magnesia Rods in Place of Platinum Wire.**—E. Wedekind.—The author has found that little rods of magnesia about 1 mm. thick can be used instead of platinum wire in analytical work. The material is not pure magnesia, but the substance which is used for the supports of incandescent mantles. It is very resistant and can be used for flame tests and for borax beads. Small quantities of substances can be fused or volatilised on it, as on platinum foil.

**Dibenzyl and Diphenyl Silicols and Silicones.**—Geoffrey Martin.—The author has prepared dibenzyl silicone,  $\text{SiO}(\text{CH}_2\text{C}_6\text{H}_5)_2$ , by exposing a solution of dibenzyl silicol in caustic potash to the action of the carbon dioxide of the air for several days. Diphenyl silicol can be obtained by allowing diphenyl silicon chloride to drop into dilute ammonia or water. From it a diphenyl silicon can be prepared by heating to 140° and extracting with caustic potash solution containing methyl alcohol.

**Mirror-image Isomerism in Iron Compounds.**—A. Werner.—The tri-*a*-dipyridyl iron salts can be split into their mirror-image isomers by means of ammonium tartrate. The rotatory power of *l*-tri-*a*-dipyridyl iron tartrate is very great, but it very rapidly undergoes racemisation, probably because the salt gives up *a*-dipyridyl, and then remains in dynamic equilibrium with it.



## MISCELLANEOUS.

**Royal Society of Arts.**—A Short Course of Four Lectures on "Heavy Oil Engines," by Captain H. Riall Sankey, R.E. (ret.), M.Inst.C.E., will be given before the Royal Society of Arts, under the Howard Bequest, commencing on Monday evening, the 29th inst., at 8 p.m. Admission to the lectures is free to non-members of the Society on production of a Member's order, or by the personal introduction of a Member. The following is a syllabus of the lectures:—

**LECTURE I.**—April 29.—The oil engine is an internal combustion engine—Difference between light and heavy oil engines—Difference between Diesel and other heavy oil engines—Brief history of the Diesel engine—Theoretical thermal efficiency—Heat and other losses—Actual thermal efficiency—Efficiency ratio—Thermal efficiency compared with other internal combustion engines and with external combustion engines—Cycle of operation of a 4-stroke and of a 2-stroke Diesel engine, and essential parts to produce these cycles.

**LECTURE II.**—May 6.—Various types of Diesel engines—Considerations affecting design—Design of various parts, such as cylinders, valves, pistons, connecting rods, crankshafts, frames, air compressors, &c., for 4-cycle and for 2-cycle engines—Materials used for the various parts—Number and arrangement of cylinders for vertical and horizontal engines.

**LECTURE III.**—May 13.—Description of Diesel engines manufactured by various makers—Sizes in current manufacture and future possibilities—Speeds and weight for land and marine engines—Various kinds of oil available for Diesel engines; their characteristics, calorific value, and sources of supply.

**LECTURE IV.**—May 20.—Economic results in respect of fuel and of total annual cost—Comparison of Diesel, gas, and steam engines, in respect of capital cost, fuel cost, and total annual cost—Various applications to land and marine purposes—Other heavy oil engines—Semi-Diesel engines.

## MEETINGS FOR THE WEEK.

**MONDAY, 29th.**—Royal Society of Arts, 8. (Howard Lecture). "Heavy Oil Engines," by Capt. H. R. Sankey, R.E.

**TUESDAY, 30th.**—Royal Institution, 3. "Insect Distribution, with special reference to the British Islands," by F. Balfour Browne, M.A.

**WEDNESDAY, May 1st.**—Royal Society of Arts, 8. "Ancient Egyptian Ceramics," by William Burton, M.A.

— Society of Public Analysts, 8. "Analysis of Lithopone," by W. L. Austin and C. A. Keane.

— "Effect of Calcium on the Ammonium Molybdate Lead Assay," by C. O. Bannister and W. McNamara. "Constituents of Oil of Savin," by I. Watson Agnew and R. B. Croad. "Detection of Heavy Petroleum in Paints and Vegetable Oils," by W. B. Pollard.

— Royal Institution, 5. Annual Meeting.  
**THURSDAY, 2nd.**—Royal Institution, 3. "Recent Explorations in the Canadian Rocky Mountains," by Prof. J. Norman Collie, F.R.S., &c.

— Royal Society. "Petrifications of the Earliest European Angiosperms," by Marie C. Stopes. "Distribution of Oxydases in Plants and their Role in the Formation of Pigments," by F. Keeble and E. F. Armstrong. "Manifestation of Active Resistance to the Growth of Implanted Cancer," by B. R. G. Russell. "Nature of the Immune Reaction to Transplanted Cancer in the Rat," by W. H. Woglom. "Instability of a Cortical Point," by T. G. Brown and C. S. Sherrington. "Measurement of *Trypanosoma rhodesiense*," by J. W. W. Stephens and H. B. Fantham.

— Chemical, 8.30. "Nor-hyoscyamine and Nor-atropine, Alkaloids occurring in various Solanaceous Plants," by F. H. Carr and W. C. Reynolds. "Researches on the Constitution of Physostigmine," by A. H. Salway. "The 'True' Ionisation and Hydration Constants of Ammonia and some Amines, with a Note on the Formulation of Nitrogen Compounds," by T. S. Moore.

**FRIDAY, 3rd.**—Royal Institution, 9. "The Use of Pedigrees," by W. C. Dampier Whetham, F.R.S.

**SATURDAY, 4th.**—Royal Institution, 3. "The [Architecture of the Renaissance in France," by Reginald Blomfield.





DEVITRIFICATION OF SILICA GLASS.—SIR WILLIAM CROOKES, O.M., &c.



FIG. 1.

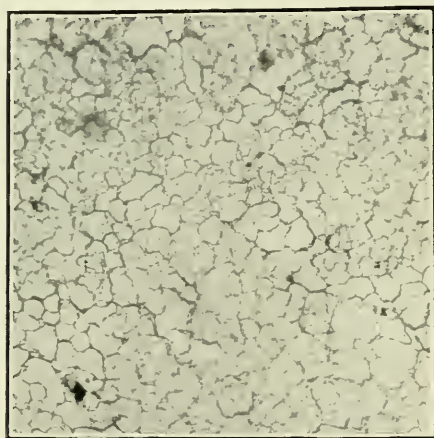


FIG. 2.

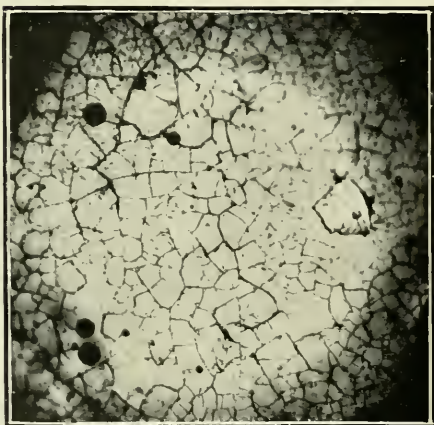


FIG. 3.



# THE CHEMICAL NEWS.

VOL. CV., No. 2736.

## ON THE DEVITRIFICATION OF SILICA GLASS.\*

By Sir WILLIAM CROOKES, O.M., For. Sec. R.S.

THE use of apparatus blown and worked from melted quartz is now almost universal in chemical laboratories, especially where temperatures are required above the heat at which glass softens.

When working at fairly high temperatures I was inconvenienced by the leakage of air through silica glass.† The apparatus (Fig. 1) was in the form of a perfectly clear and transparent tube, 1 cm. diameter and 20 cm. long, with a bulb  $2\frac{1}{2}$  cm. diameter blown on the end. The other end of the silica tube was drawn out for connecting with the pump and sealing. It was exhausted to a high vacuum and heated to near redness along its whole length to remove any gas that might be condensed on the walls—it was then sealed off.

The tube was placed bulb uppermost in an electric resistance furnace in such a position that the bulb would be at the point of greatest heat, the lower part of the tube remaining comparatively cool; it was kept at a temperature of  $1300^{\circ}$  for twenty hours, at the end of which time the silica tube was removed from the furnace. The long continued high temperature caused the bulb and the upper part of the tube to devitrify, and become white and translucent like frosted glass. The sealed-off end was carefully opened, and it was apparent that the inrush of air was by no means so strong as it would have been had the vacuum been as perfect as it was when the tube was sealed up.

This looked as if there had been a considerable amount of leakage through the devitrified bulb, and I tried a test experiment. The tube was again attached to the Sprengel pump, and exhausted to as high a point as possible. During the progress of exhaustion, when the pump was rattling with the characteristic sound of a high vacuum, a large and powerful Bunsen flame was used to heat the bulb. Not the least difference in the sound could be distinguished. When the vacuum was at its highest the tube was sealed off, it was put into the electric furnace, and kept at a temperature of  $1300^{\circ}$  for eleven hours. After cooling the end of the tube was broken off under mercury. The mercury rose, but did not fill the bulb. The amount that entered was measured, and found to be 17.75 cc. Afterwards the tube and bulb were completely filled with mercury, the whole again measured, and the capacity of the tube and bulb was found to be 19.25 cc., showing that 1.5 cc. of gas, or 7.79 per cent of the tube's capacity, had leaked through the devitrified silica in eleven hours at  $1300^{\circ}$ .

To ascertain if air would leak through the devitrified silica at the ordinary temperature a fac-simile of tube and bulb was made in glass, and the two tubes were simultaneously exhausted on the pump. They were both heated, allowed to cool, and sealed off at the same time. The silica and glass tubes were put in the balance case and kept there for some time. When they were both at uniform temperature the silica tube was weighed. The tube and weights not being moved in the meantime, weighings were taken hourly, the balance being untouched during the intervals. In eighteen hours the weight increased 0.048 grain.

After the silica and glass tubes had been at rest for some days they were opened simultaneously under mercury. The

glass tube filled at once, only a microscopic bubble of air remained at the top. The silica tube, on the contrary, only partially filled, and on measuring the mercury that entered it amounted to 10.15 cc., the capacity of the tube being 19 cc. Therefore in a few days air to the amount of 46.58 per cent of the total capacity of the apparatus had leaked in.

A micro-photograph was taken of the surface of the devitrified silica bulb (Fig. 2). It showed a surface cracked all over into the appearance of cells, and on closer examination many of the cells showed decided hexagonal outline.

I observed a similar appearance a few years ago when a silica dish, originally clear and transparent as glass, was used for evaporating down about 100 mgrms. of pure radium bromide. Patches appeared on the bottom having a dull roughened appearance, and on examination under the microscope the appearance was very similar to the surface of the devitrified silica bulb just described (Fig. 3). The appearances are so alike that it is legitimate to assume that the same cause had been at work, and that devitrification of the surface is produced both by exposure to a very high and long continued temperature and to the contact with a radium salt at a temperature of boiling water. I have not seen this effect on the surface of glass or silica bottles in which radium salts have been kept in the cold for some years.

## A NEW AND ACCURATE METHOD FOR DETERMINING THE TRYPTIC VALUE OF PANCREATIN.\*

By CLARENCE F. RAMSAY.

At the present time very little attention is being paid to pancreatin as regards its proteolytic activity. This is probably due to the fact that no satisfactory test has been proposed by which it might be ascertained just how much proteid a given sample of pancreatin will digest.

The tryptic value of pancreatin should be taken into account, for it is more energetic than pepsin. In the case of pepsin considerable time is necessary for proteid to be converted into peptone, while trypsin converts proteids rapidly into proteoses and peptone. It has been stated that trypsin is so energetic that it will convert proteid beyond the stage of peptone into leucin, tyrosin, and other amides.

The U.S.P. method for determining the tryptic power of pancreatin is very indefinite and uncertain because of the manner of testing the end reaction. It states that by adding a little nitric acid to a portion of the peptonised milk no coagulation should occur. As regards the word coagulation in this test there is a difference of opinion. If we are to think of coagulation as the result obtained when adding rennin to milk it would be better to call this separation a precipitation. The result depends altogether upon the amount of acid added. If a minute quantity of acid is added, no precipitate is formed, while with more acid there is a decided precipitation. A large excess of acid generally results in solution of the precipitate. Acid will cause a precipitation in peptonised milk no matter how long the digestion takes place.

In view of the importance of trypsin in pancreatin the writer wishes to propose a milk test which, if carried out exactly in accordance with directions, will give very accurate results. In testing the activity of enzymes, it is very important to adhere to certain conditions, such as temperature, time for digestion, &c. So it is in testing trypsin. This test determines the amount of pancreatin necessary to peptonise a given quantity of milk in fifteen minutes. The end reaction is determined by adding a

\* A Paper read before the Royal Society, March 7, 1912.

† Jaquero and Perrot have shown that fused silica is permeable to helium and hydrogen at a low red heat. (*Comptes Rendus*, cxxxix., 789, Nov., 1904; and cxliv., 135, Jan., 1907).

\* Read before the American Chemical Society. From the *Journal of Industrial and Engineering Chemistry*, iii., No. 11.

slightly acidified solution of rennin to a portion of the peptonised milk and noting if precipitation or coagulation takes place. The final end-point of the test is reached when the milk is just sufficiently peptonised so that it will not be coagulated by the rennin. To determine this it is necessary to test the pancreatin first at wide ranges of strength, say, 1 to 700, 1 to 800, 1 to 900, &c. By this is meant 1 grm. of pancreatin to 700 cc. of milk. After it is found between what wide ranges the strength of the pancreatin lies, a second series of tests are made at intermediate values until the exact strength of the pancreatin is found. In carrying out the test it was found necessary to make the milk slightly alkaline with sodium bicarbonate to prevent the pancreatin from curdling the milk. This coagulation is probably due to the presence of an enzyme in pancreatin similar to rennin.

The materials required for the test are as follows:—

0.5 grm. pancreatin added to sufficient distilled water to make 50 cc. of solution.

900 cc. of milk containing 1.8 grms. of sodium bicarbonate.

2 grms. of rennin (1 : 30,000 in ten minutes or equivalent) and 1 cc. of 6 per cent acetic acid (U.S.P.) added to 50 cc. of distilled water.

After warming the milk, place exactly 50 cc. in a cylindrical tube of about 100 cc. capacity. Prepare several such tubes and place in a water-bath, maintaining the temperature at 40° C. Add to the tubes of milk the following amounts of the pancreatin solution:—

|      |    |    |    |           |
|------|----|----|----|-----------|
| Cc.  |    |    |    |           |
| 8.33 | .. | .. | .. | (1 : 600) |
| 7.69 | .. | .. | .. | (1 : 650) |
| 7.14 | .. | .. | .. | (1 : 700) |
| 6.66 | .. | .. | .. | (1 : 750) |
| 6.25 | .. | .. | .. | (1 : 800) |

In each case note the exact time when the pancreatin is added, mix well, and after digesting fifteen minutes place 5 cc. of the digested milk in a test-tube, add 3 cc. of the rennin solution, and shake well. No precipitate indicates that the casein has all been peptonised, and that the pancreatin is stronger than the strength tested. For example, if there was no precipitation at 1 : 700, but there was a precipitation at 1 : 750, then it would be necessary to run more digestions between 1 : 700 and 1 : 750. Make a fresh solution of pancreatin, and use the following amounts:—

|      |    |    |    |           |
|------|----|----|----|-----------|
| Cc.  |    |    |    |           |
| 7.04 | .. | .. | .. | (1 : 710) |
| 6.94 | .. | .. | .. | (1 : 720) |
| 6.84 | .. | .. | .. | (1 : 730) |
| 6.75 | .. | .. | .. | (1 : 740) |

In this manner it can be determined quite accurately how many times its own weight of milk a given sample of pancreatin will peptonise. In order to get accurate results the test must be carried out strictly in accordance with directions. As stated above acid will precipitate peptonised milk; therefore just enough acid is added to the rennin solution so that 3 cc. of this solution will neutralise the sodium bicarbonate in 5 cc. of the peptonised milk. Then the rennin will do its work, for it will not form the precipitate in an alkaline solution.

Attention must be called to the fact that pancreatin in a neutral solution deteriorates quite rapidly. Therefore this solution should be made up the last thing so that it can be added immediately to the milk. The amount of pancreatin solution suggested is sufficient for testing the strengths as indicated.

It must be borne in mind that all tests of this nature are purely arbitrary; consequently a slight variation in the carrying out of such a test would give different results. The method gives accurate results to within 2 or 3 per cent, which is closer than pepsin can be tested on egg albumen, and equal to the accuracy of the starch methods for testing diastases. If this proposed test is carried out

as indicated it will undoubtedly prove very satisfactory, and will make it possible for one to know the exact proteolytic activity of a sample of pancreatin.

In testing various commercial samples of pancreatin by the above test the following results were obtained:—

|     |    |    |    |          |
|-----|----|----|----|----------|
| No. |    |    |    |          |
| 1.  | .. | .. | .. | 1 : 280  |
| 2.  | .. | .. | .. | 1 : 120  |
| 3.  | .. | .. | .. | 1 : 130  |
| 4.  | .. | .. | .. | 1 : 670  |
| 5.  | .. | .. | .. | 1 : 850  |
| 6.  | .. | .. | .. | 1 : 1450 |
| 7.  | .. | .. | .. | 1 : 1750 |
| 8.  | .. | .. | .. | 1 : 1200 |
| 9.  | .. | .. | .. | 1 : 960  |

It will be noted that there is a wide variation in the tryptic value of commercial pancreatins. The writer suggests if the above tests meet with favour in the hands of other workers, it may serve as the basis for the official assay of the U.S.P. From the above examination of commercial pancreatins it would appear that a requirement of 1 to 800 or 1 to 1000 would be a fair standard.

#### A NOTE ON THE ASSAY OF FORMALDEHYDE.\*

By ELIAS ELVOVE.

(Concluded from p. 202).

ON now repeating these experiments in exactly the same way except that the excess of KCN was increased to approximately one-half of an equivalent (using 48 cc. of N/10 KCN, whose factor was 0.9875), the results shown in Table III. were obtained.

TABLE III.—Effect of Varying the Temperature.

| No. of experiment.     | Amount of formaldehyde solution taken. Cc. | Amount of N/10 KCN added. (a) Cc. | Amount of N/10 AgNO <sub>3</sub> used. Cc. | N/10 KCNS required for one-half of filtrate. Cc. | Found equivalent of the formaldehyde solution in terms of N/10 AgNO <sub>3</sub> . Cc. |
|------------------------|--------------------------------------------|-----------------------------------|--------------------------------------------|--------------------------------------------------|----------------------------------------------------------------------------------------|
| (Temperature, 5° C.).  |                                            |                                   |                                            |                                                  |                                                                                        |
| 1                      | 25                                         | 33                                | 5                                          | 1.90                                             | 31.50                                                                                  |
| 2                      | 25                                         | 40                                | 12                                         | 2.30                                             | 32.23                                                                                  |
| 3                      | 25                                         | 48                                | 20                                         | 2.38                                             | 32.32                                                                                  |
| (Temperature, 15° C.). |                                            |                                   |                                            |                                                  |                                                                                        |
| 4                      | 25                                         | 33                                | 5                                          | 1.83                                             | 31.32                                                                                  |
| 5                      | 25                                         | 40                                | 12                                         | 2.30                                             | 32.18                                                                                  |
| 6                      | 25                                         | 48                                | 20                                         | 2.40                                             | 32.30                                                                                  |
| (Temperature, 30° C.). |                                            |                                   |                                            |                                                  |                                                                                        |
| 7                      | 25                                         | 33                                | 5                                          | 1.60                                             | 30.86                                                                                  |
| 8                      | 25                                         | 40                                | 12                                         | 2.20                                             | 31.98                                                                                  |
| 9                      | 25                                         | 48                                | 20                                         | 2.40                                             | 32.30                                                                                  |
| (Temperature, 40° C.). |                                            |                                   |                                            |                                                  |                                                                                        |
| 10                     | 25                                         | 33                                | 5                                          | 1.35                                             | 30.36                                                                                  |
| 11                     | 25                                         | 40                                | 12                                         | 2.15                                             | 31.88                                                                                  |
| 12                     | 25                                         | 48                                | 20                                         | 2.30                                             | 32.10                                                                                  |

(a) 48 cc. of the KCN solution was equivalent to 47.56 cc. N/10 AgNO<sub>3</sub> in Exps. 1–3; to 47.5 cc. N/10 AgNO<sub>3</sub> in Exps. 4–12.

These results, therefore, like the results given in Table II., show that when only a comparatively small excess of the KCN is used, the effect of a considerable variation in the temperature manifests itself quite markedly in the results, but when the excess of KCN is increased to about



one-half of an equivalent, the results obtained at 40° C. are only slightly lower than those obtained at 5° C.; while the results given in Table III. show that a variation of the temperature between 5° C. and 30° C. had no appreciable effect on the found value of the formaldehyde solution when the excess of KCN was about one-half of an equivalent. We may conclude therefore that the ordinary changes in room temperature during the year will not appreciably affect the results when the excess of KCN is as much as one-half of an equivalent.

A closer examination of the potassium cyanide method seemed to show also that there is nothing inherent in the basic principle of this method which would prevent its application directly to the concentrated formaldehyde solutions. That such is really the case may be seen from the following experiment:—To 0.5505 grm. of a sample of U.S.P. formaldehyde, weighed out in a closely fitting glass-stoppered Erlenmeyer flask of about 150 cc. capacity, there were added 100 cc. of an approximately N/10 KCN solution, and the two solutions well mixed. This mixture was then added to a mixture of 35 cc. N/10 AgNO<sub>3</sub> and 20 cc. 10 per cent nitric acid in a 200 cc. measuring flask, the Erlenmeyer well washed, and the washings added to the silver solution, the whole made up to 200 cc., thoroughly shaken, and filtered through a dry filter. 100 cc. of this filtrate were found to require 2.00 cc. N/10 KCNS. This would make the formaldehyde in the 0.5505 grm. of the sample equivalent to 67.75 cc. N/10 AgNO<sub>3</sub>, which would correspond to 0.20325 grm. HCHO, or 36.92 per cent. On analysing a diluted solution of this sample, the result obtained corresponded to 36.98 per cent. It is thus seen that not only is the potassium cyanide method applicable to concentrated formaldehyde solutions by previously diluting them with water, but that it may even be applied to the concentrated solution directly, just as in the case of the hydrogen peroxide method.

It has already been pointed out above that in the case of the concentrated formaldehyde solution the H<sub>2</sub>O<sub>2</sub> method seems to be most generally favoured, and that it is the official method of the present U.S. Pharmacopœia. We may therefore ask, What advantages has the H<sub>2</sub>O<sub>2</sub> method over other methods, such as the iodometric or Legler method, which entitle it to this preference? The answer to this may be found partly in the results of Williams (*Journ. Am. Chem. Soc.*, 1905, p. 600), who found that in the presence of small amounts of ethyl alcohol, paraldehyde, methyl alcohol, or acetone, the H<sub>2</sub>O<sub>2</sub> method gave normal results, whereas the results obtained by the iodometric method were abnormal. Similarly, in the case of a formaldehyde solution which contained a small amount of acetaldehyde, the result obtained by the Legler method was 47.8 per cent instead of 34.87 per cent in the absence of the acetaldehyde, thus increasing the result in percentage by 12.93; whereas by the H<sub>2</sub>O<sub>2</sub> method, under similar conditions, the increase in the percentage was only 2.78 (from 35.82 to 38.6). The results of Williams, however, while showing that the H<sub>2</sub>O<sub>2</sub> method is more advantageous than the iodometric or Legler methods, also show that the KCN method is even more reliable than the H<sub>2</sub>O<sub>2</sub> method. For not only were the results by the KCN method normal in all cases where the H<sub>2</sub>O<sub>2</sub> method gave normal results, but even in the presence of acetaldehyde which, as already noted, increased the results by the H<sub>2</sub>O<sub>2</sub> method from 35.82 to 38.6 per cent, the result obtained by the KCN method was only slightly higher than in the absence of the acetaldehyde, being 35.12 per cent in the absence of the acetaldehyde and 35.3 per cent in its presence; while according to Romijn very exact formaldehyde determinations may be obtained by the KCN method even in the presence of formaldehyde, acetone, or benzaldehyde ("Die Cyankaliummethode gestattet als auch bei Anwesenheit von Acetaldehyd, beziehungsweise Aceton oder Benzaldehyd, eine sehr genaue Bestimmung des Formaldehyds," *Zeit. Anal. Chem.*, 1905, xliii., 22). We thus see that not only has the KCN method the advantage

over the H<sub>2</sub>O<sub>2</sub> method in that the reaction on which the former method is based is characteristic for aldehyde, but that it may even be used for distinguishing and determining formaldehyde in the presence of certain other aldehydes. The fact also that in the H<sub>2</sub>O<sub>2</sub> method the results will be influenced by any substance which, on oxidation under the conditions of the method, will produce acid products capable of consuming a portion of the alkali present, has led Fresenius and Grünhut (see Note) to recommend that in assaying commercial formaldehyde by the H<sub>2</sub>O<sub>2</sub> method the results obtained should be confirmed by the iodometric method, since it is only when both methods give closely agreeing results that the mean of the two may be taken to represent the actual amount of formaldehyde in the solution.

(NOTE.—"Wir sind immer dafür eingetreten, diese beiden Arbeitsweisen bei der Handelsanalyse, insbesondere bei der Schiedsanalyse, neben einander zu benutzen und das Mittel der nach beiden Verfahren erhaltenen und hinreichend übereinstimmenden Werte als den wahren Formaldehydgehalt anzusehen. Diese Forderung, zwei verschiedene Methoden anzuwenden, beruht darauf, dass beide nicht eigentlich auf die directe Bestimmung des Formaldehyds abzielen, ihn als nicht in einer wohlcharakterisierten und leicht zu identifizierenden Verbindungsform abscheiden. Beide benutzen viel mehr Reactionen, die ausser dem Formaldehyd noch sehr viele andere Verbindungen zeigen können: die eine lässt alle Substanzen finden, die in alkalischer Lösung durch Wasserstoffsuperoxyd zu Säuren oxydiert werden, die andere alle die jengien, die in alkalischer Lösung durch Jod oxydiert werden oder in anderer Weise Jod verbrauchen, ohne es beim Ansäuern weider frei zu geben."—*Zeit. Anal. Chem.*, 1905, xliv., 15).

But these are not the only disadvantages of the H<sub>2</sub>O<sub>2</sub> method. For, according to Smith (*Journ. Am. Chem. Soc.*, 1903, xxv., 1034), the "working range" of the H<sub>2</sub>O<sub>2</sub> method on the lower end ends with solutions containing about 5 per cent HCHO; so that when we have occasion to carry out comparative experiments requiring a knowledge of the formaldehyde content of the strong solutions, and also of solutions which contain considerably less than about 5 per cent formaldehyde, if we would use the H<sub>2</sub>O<sub>2</sub> method we would be obliged to use two different methods in the same work. Therefore, should we not prefer a method (the KCN method) which can be universally applied to formaldehyde solutions, whether these be strong or weak with reference to their formaldehyde content, and which is based on a reaction that is characteristic of aldehyde, and also permits of distinguishing and estimating formaldehyde in the presence of certain other aldehydes? Finally, we may add that the KCN method has also the advantage of being based ultimately on the beautiful and exact Volhard thiocyanate method, and that the silver nitrate solution required comes nearest to the chosen ultimate standard for volumetric solutions—pure metallic silver (Elvove, *Am. Journ. Pharm.*, 1910, lxxii., 203).

In connection with the study of embalming fluids to which reference has already been made, it was desired also to obtain an idea as to degree of variation in the strength of the commercial formaldehyde on the American market. Accordingly, samples were obtained from the principal American firms who sell this article. And inasmuch as, for the reasons given above, the KCN method may be considered as more reliable for determining the actual formaldehyde content of such solutions, the determinations were carried out by this method. Seven samples were examined. The results obtained are given in Table IV.

The results given in Table IV. show that the majority of the samples examined contained slightly less formaldehyde than is required by the present U.S.P. ("not less than 37 per cent by weight"), and that only two (Nos. 6 and 7) of the seven samples examined may be said to have come up to its requirement. Similar results have also been obtained by Evans, Sons, Lescher, and Webb ("Analytical Notes," 1907-1908, p. 22), who found that

TABLE IV.—Showing the HCHO Strength of Various Samples of Commercial Formaldehyde.

| No. of sample | Amount of formaldehyde solution taken (a). |     | Amount of N/10 KCN added (b). |      | Amount of N/10 AgNO <sub>3</sub> used. |       | N/10 KCNS required for one-half of filtrate. |     | Found equivalent of the formaldehyde solution in terms of N/10 AgNO <sub>3</sub> . |     | Amount of HCHO expressed in percentage by weight. |           |
|---------------|--------------------------------------------|-----|-------------------------------|------|----------------------------------------|-------|----------------------------------------------|-----|------------------------------------------------------------------------------------|-----|---------------------------------------------------|-----------|
|               | Cc.                                        | Cc. | Cc.                           | Cc.  | Cc.                                    | Cc.   | Cc.                                          | Cc. | Cc.                                                                                | Cc. | Per cent.                                         | Per cent. |
| 1             | 25                                         | 48  | 20                            | 1.75 | 31.10                                  | 35.47 |                                              |     |                                                                                    |     |                                                   |           |
| 2             | 25                                         | 48  | 20                            | 2.05 | 31.74                                  | 36.11 |                                              |     |                                                                                    |     |                                                   |           |
| 3             | 25                                         | 48  | 20                            | 2.00 | 31.64                                  | 36.21 |                                              |     |                                                                                    |     |                                                   |           |
| 4             | 25                                         | 48  | 20                            | 2.30 | 32.25                                  | 36.53 |                                              |     |                                                                                    |     |                                                   |           |
| 5             | 25                                         | 48  | 20                            | 2.35 | 32.34                                  | 36.61 |                                              |     |                                                                                    |     |                                                   |           |
| 6             | 25                                         | 48  | 20                            | 2.40 | 32.44                                  | 36.98 |                                              |     |                                                                                    |     |                                                   |           |
| 7             | 25                                         | 48  | 20                            | 2.91 | 33.46                                  | 37.97 |                                              |     |                                                                                    |     |                                                   |           |

(a) These solutions of formaldehyde contained the following amounts in grms. of the respective samples of the concentrated formaldehyde in 2000 cc.:—No. 1, 21.0418; No. 2, 21.0958; No. 3, 20.9690; No. 4, 21.1879; No. 5, 21.2005; No. 6, 21.0512; No. 7, 21.1459.

(b) The found value of the KCN solution was as follows:—In the case of No. 1, 48 cc. was equivalent to 47.6 cc. N/10 AgNO<sub>3</sub>; in No. 4 to 47.65; and in the remainder to 47.64 cc. N/10 AgNO<sub>3</sub>.

the nine samples of commercial formaldehyde solution which they examined ranged from 37 down to 35.4 per cent of absolute formaldehyde by weight. Likewise, Bachman (*Proc. Minnesota Pharm. Ass.*, 1907, p. 41; from *Bull.* No. 63, Hyg. Lab., U.S. Pub. Health and Mar. Hosp. Serv., Wash., p. 295) reports solution of formaldehyde ranging from 36.6 per cent to 31.8 per cent, instead of the minimum of 37 per cent as required by the present U.S.P. Finally, we may mention in this connection that the formaldehyde requirement of the French Pharmacopœia (1908), and also of the German Pharmacopœia (1910), is only 35 per cent by weight of absolute formaldehyde. On the other hand, with the exception of only one sample (No. 1), all contained more than 36 per cent by weight of absolute formaldehyde. Therefore, bearing in mind the comparative difficulty of manufacturing and keeping unaltered solutions of formaldehyde of considerably higher concentration than the minimum of the present U.S.P., and also that by making the U.S.P. requirement more in harmony with these latter pharmacopœias and with what seems to be the actual condition of the American market, it would not mean that the purity requirement will be lowered, but only that the solution will be just a little less concentrated; it would seem advisable that the formaldehyde requirement, in the next revision of the U.S.P., be changed from the present minimum of 37 per cent to a minimum of 36 per cent by weight of absolute formaldehyde. Also that the KCN method might with advantage be substituted for the present H<sub>2</sub>O<sub>2</sub> method. The KCN method, applied to U.S.P. solution of formaldehyde, may be carried out as follows:—

Transfer 0.5 cc. of the sample of solution of formaldehyde to a well-stoppered Erlenmeyer flask of about 150 cc. capacity, and determine its weight. Add to it immediately 100 cc. of a solution of potassium cyanide of a strength close to tenth-normal (6.5 grms. KCN to 1000 cc.), the exact strength of which is known. Mix well, and add to a mixture of 40 cc. N/10 silver nitrate, and 10 cc. of dilute (10 per cent) nitric acid, in a 200 cc. measuring flask. Wash the Erlenmeyer flask, adding the washings to the silver solution, and make up the whole to 200 cc. Shake thoroughly, filter through a dry filter, and titrate the excess of silver in 100 cc. of the filtrate by means of N/10 ammonium or potassium sulphocyanate, using ferric alum as indicator. The number of cc. of N/10 sulphocyanate found to require, multiplied by 2, and the product subtracted from 40, will give the equivalent of the uncombined KCN in cc. of N/10 AgNO<sub>3</sub>. Subtracting this from the corresponding equivalent of the total KCN added, multi-

plying the difference by 0.3, and dividing this product by the weight of the sample taken, the quotient will represent the percentage by weight of absolute formaldehyde in the sample.

#### A SHORT METHOD FOR THE DETERMINATION OF SOLUBLE ARSENIC IN COMMERCIAL LEAD ARSENATES.

By B. E. CURRY and T. O. SMITH.

As the result of a request for an immediate report on the amount of soluble free arsenic oxide in a sample of commercial lead arsenate, the writers began a series of experiments to develop a method of analysis which would give satisfactory results without incurring the tedious shaking of 2 litre bottles, eight times daily for ten days as in the procedure outlined in the standard A.O.A.C. method for this determination.

Since it was desired mainly to reduce the time, the method which naturally suggested itself was one of determining the amount of continuous stirring at room temperature, that would be equivalent to the eighty shakings at intervals during ten days. Accordingly, the samples were placed in a thermostat at 20° C., and stirred continuously by means of a hot-air engine.

In order that the results might be directly comparable with the results obtained by the A.O.A.C. method it was necessary to use 2 litre bottles, or less than 2 gm. samples of lead arsenate. The thermostat available would not conveniently carry bottles with a capacity of more than 500 cc., and it did not seem advisable to use less than 2 gm. samples.

A few preliminary determinations demonstrated that more than eighteen hours of continuous stirring did not appreciably increase the amount of arsenic oxide in solution. Also, these results showed that no obvious direct relation existed between the A.O.A.C. results and those obtained by continually stirring 2 gm. samples in the thermostat with 500 cc. of water. The solubility of the lead arsenate itself entered in, and caused the difference between results obtained by the two methods. The difference in the volumes of water used in the two methods amounted to 1500 cc. This quantity of water dissolves a considerable amount of lead arsenate.

This consideration involved a side problem. It has been pointed out by others that arsenate of lead may mean the triplumbic arsenate, Pb<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub>, or plumbic hydrogen arsenate, PbHAsO<sub>4</sub>. Most commercial samples may consist of a mixture of these two, the amount of each depending upon the method and the conditions under which the precipitation was made. It is evident, also, that in some cases the by-products formed in the process of manufacture have not been washed out. In some samples the odour of acetic acid, which is formed when lead arsenate is made from lead acetate and disodium arsenate, would indicate that this step in the manufacture had probably gone no farther than the filter-press.

Based on the theoretical percentage of As<sub>2</sub>O<sub>5</sub> in lead arsenates consisting of mixtures of Pb<sub>3</sub>(AsO<sub>4</sub>)<sub>2</sub> and PbHAsO<sub>4</sub>, and also upon the analysis of a number of samples from some of the leading manufacturers, it is evident that most commercial grades carry from 25 to 33 per cent of As<sub>2</sub>O<sub>5</sub> in the moisture-free product. As the solubility of these lead arsenates is low the variation within these limits is slight, and a solubility factor may be determined which introduces no appreciable error within this range.

Lead arsenate is generally put on the market in airtight containers in order to keep it in a moist condition until ready for use. After it has once been dried it is much more difficult to keep in suspension. This fact suggested the relative rate of solubilities of the dry arsenate and the commercial form which usually contains about 40 per cent to 60 per cent moisture. Investigation showed that the



moist sample reached its maximum solubility in about eighteen hours, while the dry sample required several days. Because of this difference in the rate of solubility it is better to determine the water, and then weigh out an amount of the moist sample equivalent to 2 grms. of dry lead arsenate. All the following determinations were made on moist samples. To overcome the inconvenience of washing the moist sample from a weighing tube or watch-glass, a small piece of oiled-paper may be balanced on the pan. The sample is weighed on this paper, and the paper then transferred to the jar. It is necessary to stir the sample well into suspension with a glass rod before placing the jar in the thermostat.

Several experiments were made to determine the time required to bring the lead arsenate and water into equilibrium. It was found that with the temperature at 20° C. the maximum time was for all practical purposes not more than eighteen hours. Satisfactory results were had where stirring had been continued only twelve hours. This makes it easily possible to complete the determination the second day. By the A.O.A.C. method the report is delayed until the eleventh day.

When 500 cc. jars are used as in these experiments, a 200 cc. portion of the solution is a satisfactory amount for analysis. Most lead arsenate solutions do not subside rapidly. In order to obtain a solution free from solid lead arsenate it is usually necessary to pour the contents of the jar on a filter, and take the sample for analysis from the filtrate. In a few samples of commercial lead arsenate, small amounts of arsenious oxide were found. The exact amount may readily be determined by simply adding to this 200 cc. portion the starch and bicarbonate, and titrating with a standard iodine solution.  $As_2O_3 + 4I + 2H_2O = As_2O_5 + 4HI$ .

The addition of bicarbonate, starch, and iodine solution does not interfere with the subsequent determination of arsenic oxide. In the reduction the bicarbonate is neutralised, the starch is converted into sugar, and in the acid solution the iodine becomes a reducing agent. Since arsenious oxide is not always present, it is desirable to test it qualitatively in a part of the solution remaining after the two samples of 200 cc. each have been taken.

The reduction of the arsenic oxide to arsenious oxide in the 200 cc. sample is readily accomplished by the modified method of Mohr. In the laboratory of the New Hampshire Agricultural Experiment Station, 5 cc. of sulphuric acid and 1 gm. of potassium iodide are added to the sample in a 400 cc. beaker, and the solution boiled until the volume is reduced to 40 or 50 cc. The solution is then cooled and diluted to about 150 cc. In most cases the iodine will not all have been removed, and the solution will retain a yellow colour. This excess of iodine is removed by the addition of twentieth normal sodium thiosulphate solution added carefully from a burette.  $2I + 2Na_2S_2O_3 = Na_2S_4O_6 + 2NaI$ .

If the flask or beaker is of colourless glass and set on a white plate carefully screened from reflected colours, it is not necessary to add starch to determine the end-point. The addition of the starch here is undesirable as will be noted later, and under these conditions the disappearance of the yellow due to the presence of iodine gives a satisfactory end-point.

After the excess of iodine is removed the clear solution is made slightly alkaline. A sodium hydroxide solution is more convenient and rapid for this purpose than sodium carbonate, and gives satisfactory results. The solution is again made acid with a few drops of dilute sulphuric acid, and stirred well to make certain that all alkali is neutralised; the solution is made alkaline again with sodium bicarbonate and is ready for titration. A considerable excess of bicarbonate, as is sometimes recommended, has not been found necessary in these experiments. The solution is titrated with a standard iodine solution according to the equation given for the oxidation of free arsenious oxide in the original solution. Various comments have been made on the use of starch as an indicator in this reaction, and

many methods proposed for eliminating its objectionable features. A number of these methods were tried in these experiments. The digestion of the starch in dilute hydrochloric acid for twenty-four hours, and subsequent drying at 100° C. for three hours, is not entirely without merit, but was not found necessary when a good starch was procured and well boiled. The addition of three drops of a 10 per cent solution of potassium iodide increases the delicacy of the end-point when only a part of a cc. of iodine solution is used. When a larger amount is used the potassium iodide in the iodine solution itself serves the purpose, and makes further addition unnecessary.

In a few samples the lead was removed as sulphate before beginning the analysis for arsenic, but, with the amount of lead present in these samples, its presence was not found objectionable. The number of cases in which this was investigated, however, and the small amounts of lead present in all the samples preclude any generalisation as to how far this statement will hold true.

The results thus obtained include all arsenic oxide in solution, and are lower than those obtained by the A.O.A.C. method. This is because the solubility of lead arsenate is left out of consideration, and the volumes of water are unequal. In order to fix the relation between the results obtained by the two methods it was necessary, first, to determine the solubility of lead arsenate. Accordingly, a number of samples were prepared in the laboratory, and a number of commercial samples were selected and washed as free as possible from by-products with distilled water. The solubility of the lead arsenate in these samples was determined by stirring at 20° in the thermostat, and also by the A.O.A.C. method. It was found that the amount of soluble arsenic determined by the A.O.A.C. method was exactly four times as much as that found by the short method, the amounts being directly proportional to the volumes of water used in the different methods. The average of the results obtained by the A.O.A.C. method calculated to percentage was 0.605 per cent, while the average of the results obtained by the short method was 0.151 per cent. These results include the blank for the end-point in the titration. The results obtained by both methods agree very closely. In order to obtain the amount of soluble arsenic not in the form of lead arsenate the above percentage should be subtracted from the total amount of soluble arsenic.

Manufacturers supplied us with seventeen samples of lead arsenate which carried various amounts of soluble arsenic oxide. These samples were analysed for soluble arsenic by the short method outlined above, and also by the A.O.A.C. method. The results of these determinations are given in Table I. In this table, Column 2 gives the results obtained by the short method, Column 3 shows the results obtained by the A.O.A.C. method. No corrections are made in these columns for the solubility of lead arsenate. These results give the total percentage of soluble  $As_2O_5$ . These samples contained no soluble arsenious oxide. Column 4 shows the results obtained by the short method after subtracting the factor 0.151 per cent for the solubility of the arsenate of lead. Column 5 shows the results by the A.O.A.C. method after making the correction of 0.605 per cent. The results given in Columns 4 and 5 are practically identical.

Referring still to the table it is at once obvious that by correcting for the solubility of lead arsenate that the results determined by either method may be quickly changed to terms of the other. The corrected results obtained by the short method give only the soluble arsenic oxide uncombined with lead oxide. On this account it more truly tells the nature and quality of any commercial lead arsenate.

The A.O.A.C. method gives results uniformly 0.605 per cent higher than the corrected results given by the shorter method. Stated otherwise, when 0.605 per cent is added to the results obtained by this method, the results become the same as those obtained by the A.O.A.C. method, and with the expense of much less time. The result of this

method as given in Column 4 gives the soluble arsenic oxide not combined with lead oxide.

TABLE I.

| Lab.<br>No. of<br>sample. | Per cent of soluble arsenic. |                        | Per cent of soluble arsenic.                                     |                                                                     |
|---------------------------|------------------------------|------------------------|------------------------------------------------------------------|---------------------------------------------------------------------|
|                           | By short<br>method.          | By A.O.A.C.<br>method. | Short method<br>corrected for<br>solubility of<br>lead arsenate. | A.O.A.C. method<br>corrected for<br>solubility of<br>lead arsenate. |
| 1                         | 0·26                         | 0·70                   | 0·11                                                             | 0·10                                                                |
| 2                         | 0·37                         | 0·81                   | 0·22                                                             | 0·21                                                                |
| 3                         | 0·37                         | 0·85                   | 0·22                                                             | 0·25                                                                |
| 4                         | 0·44                         | 0·83                   | 0·29                                                             | 0·23                                                                |
| 5                         | 0·40                         | 0·85                   | 0·25                                                             | 0·25                                                                |
| 6                         | 0·40                         | 0·91                   | 0·25                                                             | 0·31                                                                |
| 7                         | 0·41                         | 0·92                   | 0·26                                                             | 0·32                                                                |
| 8                         | 0·44                         | 0·92                   | 0·29                                                             | 0·32                                                                |
| 9                         | 0·46                         | 0·96                   | 0·31                                                             | 0·36                                                                |
| 10                        | 0·66                         | 1·12                   | 0·35                                                             | 0·52                                                                |
| 11                        | 0·77                         | 1·26                   | 0·62                                                             | 0·66                                                                |
| 12                        | 0·96                         | 1·50                   | 0·81                                                             | 0·90                                                                |
| 13                        | 1·22                         | 1·79                   | 1·07                                                             | 1·19                                                                |
| 14                        | 1·42                         | 1·98                   | 1·27                                                             | 1·38                                                                |
| 15                        | 1·99                         | 2·50                   | 1·84                                                             | 1·90                                                                |
| 16                        | 2·61                         | 3·03                   | 2·46                                                             | 2·43                                                                |
| 17                        | 3·24                         | 3·78                   | 3·09                                                             | 3·18                                                                |

The method outlined in this paper gives a rapid and accurate procedure for determining soluble arsenic oxide in commercial lead arsenate. It is pointed out that the solubility of lead arsenate affects the total amount of soluble arsenic oxide, and a correction is worked out which gives the amount of soluble arsenic oxide not combined with lead oxide.—*Journal of Industrial and Engineering Chemistry*, iv., No. 3.

## PROCEEDINGS OF SOCIETIES.

### CHEMICAL SOCIETY.

*Annual General Meeting, March 25th, 1912.*

Prof. PERCY F. PRANKLAND, LL.D., F.R.S., President,  
in the Chair.

Prof. A. G. Green and Dr. G. Senter were appointed Scrutators, and a ballot was opened for the election of Officers and Council for the ensuing year.

The Report of the Council on the progress of the Society during the past twelve months was presented by the PRESIDENT; and the TREASURER made a statement as to the Society's Income and Expenditure for 1911. After some remarks with reference to the awarding of Grants from the Research Fund of the Society made by Mr. John Hughes, the Adoption of the Report of the Council, together with the Balance Sheet and Statements of Accounts for the year ended December, 31st, 1911, proposed by Prof. E. J. MILLS and seconded by Dr. A. HARDEN, was carried unanimously.

A vote of thanks to the Auditors was proposed by the TREASURER and seconded by Mr. W. MACNAB.

#### *Report of the Council.*

On December 31st, 1910, the number of Fellows was 3073. During 1911, 136 Fellows were elected, and 2 have been reinstated, the gross total being 3211. The Society has lost 31 Fellows by death; 37 have resigned; the election of 3 Fellows have become void; 1 Fellow has been elected an Honorary and Foreign Member, and 35 have been removed for non-payment of annual subscriptions.

The total number of Fellows, therefore, on December 31st, 1911, was 3104, showing a net increase of 31 over the preceding year. For the past six years the average number of newly elected Fellows has been 163, whilst the

average increase in membership has been over 60. This year the marked falling off in the number of new Fellows accounts for the small net increase.

The names of the deceased Fellows, with the dates of their election, are:—John Attfield (1862); Edward Beanes (1864); Frederic Braby (1869); Joseph Brown (1882); Carl von Buch (1877); Edward Collens (1873); Albert Cooper (1889); John Arthur Cunningham (1907); Stephen Darby (1852); Richard Hayton Davis (1872); John Greig Ferrier (1905); James Forbes (1874); Albert Harrison (1888); Alfred Henry Hoit (1904); William Hudson (1878); Leonard Parker Kinnicutt (1895); Frederick Charles Knight (1889); Isidore Bernadotte Lyon (1873); William McCowan (1875); Mervyn Herbert Nevil Story Maskelyne (1851); John Muter (1870); Ralph Henry Christopher Neville (1878); Temple Augustus Orme (1869); Lewis Buttle Ross (1870); Sir Samuel Alexander Sadler (1868); James Sharp (1885); Harry Wood Smith (1890); James Samuel Hourston Walker (1890); William Whitehouse (1889); William Williams (1892); William George Winterson (1908).

The following Fellows have resigned:—Francis Paul Armitage, William Henry Benson Baker, George Russell Beardmore, William Arthur Colebourn, George Hugh Crisp, Middleton Henry Dand, Francis Bridger Dutton, Walter Nicholas Edwards, Walter John Elliott, Bernard Scott Evans, Joseph Valentine Francies, John Lawrence van Geyzel, Archibald Melville Glass, Herbert Grime, William Peer Groves, Archie Cecil Osborn Hann, Sydney Walters Harris, John Ansted Harrison, Arthur Edwin Hill, Victor George Jackson, Edwin Charles Jee, Rudolph Lyon, William James McKerrrow, Edward Handfield Morton, Alan Edward Munby, Cyril Lawrence Norman, Georges Ponthieu, Harry James Powell, James Proude, James Bertram Russell, Henry Stanley Shelton, Charles Joseph Smith, Brenton Symons, Harold Munkman Timpany, Gustave Arthur Troye, John Watson, George Edward Welch.

The following Fellow has been elected an Honorary and Foreign Member:—John William Mallet.

The following Fellows have been reinstated by the Council, in accordance with By-law IV.:—Robert Drysdale MacKechnie, James Bertram Russell.

The Council will be glad to receive information as to the present address of the following Life Fellows who have not answered the inquiries made in the usual manner:—J. Bayne, G. W. Davey, and J. Parkinson.

The question of the misuse of the letters "F.C.S." has again been considered by the Council, and opinion of Counsel has now been received that a person using the letters "F.C.S." without authority and for the purpose of assuming wrongfully the status of a Fellow of the Chemical Society, can be restrained by injunction from so doing.

At the end of 1910 the number of Honorary and Foreign Members was 30. During 1911 the Society has had to mourn the loss of J. H. van't Hoff, A. Ladenburg, Walther Spring, and L. J. Troost; whilst on March 2nd E. Bamberger, G. Ciamician, P. H. Ritter von Groth, J. W. Mallet, and W. Nernst were elected. The number of Honorary and Foreign Members at the end of 1911, therefore, was 31.

The Council has great pleasure in offering its hearty congratulations to Mr. Edward Riley, who completed his sixtieth year of Fellowship on December 15th, and to the following, who, during the past year, attained their Jubilee as Fellows:—Major Charles Edward Beadnell, R.A.; Mr. Henry Owen Huskisson; Mr. Frederick Norrington.

During the year, 342 scientific communications were made to the Society, 265 of which have been published already in the *Transactions*, and abstracts of all have appeared in the *Proceedings*.

The volume of *Transactions* for 1911 contains 2371 pages, of which 2270 are occupied by 259 memoirs, the remaining 101 pages being devoted to the Obituary Notices, the Faraday Lecture, the Berthelot Memorial Lecture, the



Report of the International Committee on Atomic Weights, the Report of the Annual General Meeting, and the Presidential Address; the volume for the preceding year contains 270 memoirs which occupy 2601 pages.

The *Journal* for 1911 contains 5236 abstracts, which extend to 2200 pages, whilst the abstracts for 1910 numbered 4867, and occupied 2032 pages. The abstracts may be classified as follows:—

| PART I.                                                      |      | Pages. | No. of Abstracts. |
|--------------------------------------------------------------|------|--------|-------------------|
| Organic Chemistry .. .. .                                    | 1056 | 1785   |                   |
| PART II.                                                     |      |        |                   |
| General and Physical Chemistry ..                            |      | 1097   |                   |
| Inorganic Chemistry .. .. .                                  |      | 489    |                   |
| Mineralogical Chemistry .. .. .                              |      | 136    |                   |
| Physiological Chemistry .. .. .                              |      | 717    |                   |
| Chemistry of Vegetable Physiology<br>and Agriculture .. .. . |      | 343    |                   |
| Analytical Chemistry .. .. .                                 |      | 669    |                   |
|                                                              | 1144 | 3451   |                   |
| Total in Parts I. and II. ..                                 | 2200 | 5236   |                   |

The attention of authors is drawn to the notice printed on the cover of the *Journal* regarding extra copies of papers. This notice now reads:—

"7. If Authors require more than the 50 reprints allowed by the Society, they should inform the Editor at the time they send in their corrected proofs, when the extra copies will be supplied at rates which can be obtained from the Printers."

The *Transactions* for 1911 contain obituary notices of Beilstein, Erlenmeyer, Fittig, Landolt, and Menshutkin, accompanied by a portrait of each of these eminent Honorary and Foreign Members. Obituary notices appear, also, of R. Abegg, J. Campbell Brown, Michael Carteighe, O. Guttman, Sir Walter Palmer, Bart, and C. H. Greville Williams, and the Council expresses its thanks to those gentlemen who have so kindly prepared these notices.

The Faraday Lecture was delivered in the Lecture Theatre of the Royal Institution (by the courtesy of the Managers) on June 14th, by Prof. Theodore W. Richards, who took as the subject of his discourse "The Fundamental Properties of the Elements." The lecture was published in the *Transactions* for June, and an account of the speeches made at the close of the lecture will be found in the *Proceedings* (p. 177 *et seq.*).

On November 23rd the Society had the privilege of listening to an account of the life and work of Berthelot from Prof. Harold B. Dixon.

Sir Oliver Lodge has kindly consented to deliver the Becquerel Memorial Lecture in the place of Prof. Rutherford. The Berthelot and Becquerel Lectures, together with those in honour of Moissan and Cannizzaro, may enable the Council to arrange for the publication of a second volume of Memorial Lectures.

The number of Fellows elected during the early years of the Society's existence has been still further diminished by the death of Nevil Story Maskelyne, elected on June 2nd, 1851, Stephen Darby, elected on November 15th, 1852, and John Attfield, elected on January 16th, 1862. The Society was represented by Sir William Tilden and Prof. Crossley at the funeral of Dr. Attfield, and by Dr. Hugo Müller at that of Dr. Nevil Story Maskelyne.

The Council has received a portrait of Dr. John Jeffries, presented by Mr. G. H. Gabb, and a portrait of Prof. Adolf von Baeyer, presented by the Society of Dyers and Colourists. The best thanks of the Council have been accorded for these gifts, and for a generous bequest of a number of chemical works of historical interest, of which the Library contained no copy, from the family of the late Dr. W. J. Russell,

On the occasion of the Coronation of His Majesty King George V. the Council presented a Loyal Address of Congratulation (*Proc.*, p. 184). The Society co-operated with the other Societies in Burlington House in decorating and illuminating the building during the Coronation festivities.

An Address was presented to the Royal Academy of Sciences of Turin on the occasion of the Centenary Commemoration of Amedeo Avogadro (*Proc.*, p. 272). The Society has received from the Academy a copy of the Avogadro Medal, which has been placed in the Cabinet in the Library.

At the celebration of the 500th Anniversary of the Foundation of the University of St. Andrews, the Society entrusted to Sir William Tilden the presentation of an Address of congratulation (*Proc.*, p. 185).

Prof. R. Meldola and Sir William Ramsay have been nominated to represent the Society on the Council of the International Coal Smoke Abatement Exhibition to be held in London in April, 1912, and Prof. J. B. Cohen, Prof. H. B. Dixon, and Prof. A. Smithells attended on behalf of the Society the Conference of the Smoke Abatement League of Great Britain, held in Manchester in November.

The Council desires to record its appreciation of the valuable services rendered to the Society by Prof. G. T. Morgan, who, owing to his appointment to the Chair of Chemistry at the Royal College of Science, Dublin, retires from the position of Honorary Secretary, which he has held for two years.

The general invitation to the Society to attend the meetings of the Eighth International Congress of Applied Chemistry to be held in Washington and New York in September, 1912, has been accepted by the Council on behalf of the Society. Further particulars of the Congress will be announced.

The Council considered a suggestion made by Prof. Hofmann and Prof. Ruff at the request of the German Chemical Society, for the sub-division of the section of Inorganic Chemistry at the Eighth International Congress of Applied Chemistry, and resolved that:—"In the opinion of the Council of the Chemical Society, the object of the International Congress of Applied Chemistry is to bring together persons whose interests do not exactly follow the same lines; and they consider that too much sub-division of the various Sections will defeat one of the objects for which the Congress was instituted. The Council therefore, on general grounds, cannot support the proposal made by Prof. Hofmann and Prof. Ruff for consideration by the German Chemical Society."

An International Committee has been formed for the purpose of raising a memorial to the late Prof. J. H. van't Hoff, and the Treasurer will be glad to receive donations from Fellows to this fund.

The Longstaff Medal for 1912 has been awarded to Dr. H. Brereton Baker, and the formal presentation of the medal will be made at the Annual General Meeting.

The Council has made a donation of £10 to the International Commission of Publication of Annual Tables of Constants and Numerical Data, Chemical, Physical, and Technological.

During 1911, 1808 books were borrowed from the Library, as against 1918 in 1910; of these 419 were issued by post, as compared with 573 in the previous year.

The additions to the Library comprise:—171 books, 104 of which were presented, 438 periodicals (representing 237 journals), and 87 pamphlets, compared with 163 books, 431 volumes of periodicals (representing 236 journals), and 141 pamphlets last year.

These figures show a decrease of 110 in the number of books borrowed, and 54 in the number of pamphlets; whilst there is an increase of 8 in the books added, and 7 in the number of periodicals.

With the object of keeping the Library as up-to-date and representative as possible, the Council will especially welcome the gifts of works written by Fellows of the Society.

A year ago attention was called to the fact that the expenditure for 1910 had exceeded the income by £147, but that this could be traced to several causes acting simultaneously.

In spite of the notably smaller number of new Fellows elected and the consequent diminution in receipts from admission fees, the income for the year which has closed exceeds the expenditure by £235 17s. 8d., which is more than enough to compensate for the adverse balance of the previous year. The income from all sources for 1911 amounts to £7735 11s. 6d., and the total expenditure to £7499 13s. 10d., the corresponding amounts for 1910 being £7447 5s. 10d. and £7594 12s. 2d. respectively. Whilst the receipts have thus increased by £288 5s. 8d., the expenditure has been reduced by £94 18s. 4d., and this has been attained without diminishing in any way the activity and efficiency of the Society.

The Journal is a little smaller in bulk, and has cost about £30 less for printing. Our bill for "corrections" (always a very unsatisfactory and debatable item in our printers' accounts) and the average cost per page for this, grows steadily less owing to the strenuous care of the Editor, aided by the cordial co-operation of the great majority of authors with the Publication Committee and compliance with its suggestions. The exercise of greater care in the preparation of manuscript, the adoption of more concise expression, and the elimination of unnecessary experimental details would very considerably reduce the cost of the Journal, with great advantage to author and reader alike. For 1911 the cost of the Journal was £5237 13s. 7d., as against £5177 7s. 8d. for 1910, an increase of only £60 5s. 11d. Of this, £44 10s. is due to an increase in the amount of abstractors' fees, an item paid as "piece work," for which the Society most certainly gets its full value, and the Council takes this opportunity of recording its sense of indebtedness to the abstractors for their important services. In almost all other departments economies have been effected as compared with last year; on other publications about £12, the Library £17, miscellaneous expenses £8, and administrative expenses £118. These decreases amount in all to £180 17s. 5d., and the increases to £85 19s. 1d., resulting in the net diminution of expenditure stated above.

The increased profit resulting from the management of the advertisements by the Society's officers has fully justified the changes made in this department more than a year ago, since the net gain to the Society from this source is about £110, as against £75 for 1910 and £10 in 1909. This is largely due to the energy of Mr. Carr, and to the loyal support given by the Fellows of the Society and other advertisers.

The net income from the investments in the name of the Research Fund amounts to £345 1s. 8d., and this, together with returned grants to the extent of £43 16s. 8d., made the income available for distribution amongst applicants £388 18s. 4d., and as there was a balance in hand, the Council was enabled to distribute a sum of £393 10s. in forty-two grants, which varied in amount from £3 to £25.

#### ADDENDUM.

##### *International Association of Chemical Societies.*

As mentioned in the *Proceedings* (p. 132 *et seq.*), meetings of the delegates appointed by the French, English, and German Chemical Societies took place in Paris on April 25th and 26th last, at which the statutes of the Association were drafted, and subsequently ratified by the Councils of the three Chemical Societies responsible for the foundation of the Association. These statutes are printed in full in the *Proceedings*. They may, however, be briefly summarised as follows:—

The object of the Association is to form a bond of union between the several Chemical Societies of the world for the purpose of taking into consideration such matters as are of general and international interest to Chemistry.

All Chemical Societies are eligible to join the Associa-

tion. The Association is under the direction of a Council consisting of a certain number of members, and each country can only be represented on the Council by a single Chemical Society, which shall nominate three representatives.

Thus the Council constituted at the Paris Conference consisted of Profs. Behal, Haller, and Hanriot (French Chemical Society), Profs. Frankland and Meldola, and Sir Wm. Ramsay (Chemical Society), and Profs. Jacobson, Ostwald, and Wichelhaus (German Chemical Society).

The admission of representatives of any Chemical Society is subject to election by a two-thirds majority of the Council.

At the present moment the Council has the following composition:—

German Chemical Society:—Prof. W. Ostwald (President of the Association for the ensuing session, 1912), Prof. H. Wichelhaus (Vice-President), Prof. P. Jacobson (General Secretary).

The Chemical Society:—Prof. P. F. Frankland, Prof. R. Meldola (retired), Prof. Sir Wm. Ramsay. (Prof. Arthur W. Crossley has been appointed by the Council of the Chemical Society to fill the vacancy caused by the retirement of Prof. Meldola).

French Chemical Society:—Prof. Béhal, Prof. Haller, Prof. Hanriot.

Italian Chemical Society:—Prof. G. Carrara, Prof. A. Ogliastro, Prof. E. Paterno.

Russian Chemical Society:—Prof. N. S. Kurnakow, Prof. L. A. Tschugaeff, Prof. P. J. Walden.

American Chemical Society:—Dr. A. L. Day, Prof. W. A. Noyes, Prof. Th. W. Richards.

Swiss Chemical Society:—Prof. F. Fichter, Prof. Ph. A. Guye, Prof. A. Werner.

The following Societies have also joined the Association, but are as yet unrepresented on the Council:—Nederlandsche Chemische Vereeniging; Polyteknisk Forenings Kemikergruppe (Christiania); Verein Oesterreichischer Chemiker (Vienna); Kemisk Forening (Copenhagen).

At the Paris Conference it was resolved that the first work of the Association should be the appointment of Committees in each country, to whom should be entrusted the duty of drafting reports on each of the three subjects:—(a) Nomenclature of inorganic chemistry; (b) Nomenclature of organic chemistry; (c) Unification of the methods of notation of physical constants.

The following Committees have been appointed by the Council of the Chemical Society:—

Inorganic Nomenclature—Sir Wm. Ramsay (Chairman), Dr. J. C. Cain, Dr. A. Harden.

Organic Nomenclature—Prof. W. P. Wynne (Chairman), Dr. J. C. Cain, Prof. F. S. Kipping.

Physical Constants—Dr. N. T. M. Wilshire (Chairman), Dr. J. C. Cain, Prof. A. Findlay.

These Committees, as well as the corresponding ones appointed by the several foreign Chemical Societies, have already sent in reports which will form the subject of discussion by the Council of the Association at their next sessions, commencing on April 11th in Berlin.

A Vote of Thanks to the Treasurer, Hon. Secretaries, Foreign Secretary, and Council for their services during the past year was proposed by Prof. H. McLeod, seconded by Mr. S. P. U. PICKERING, and acknowledged by Prof. J. N. COLLIE:—

In presenting the Longstaff Medal for 1912 to Dr. H. BRERETON BAKER, the PRESIDENT said:—

"Dr. Brereton Baker—It is my pleasant duty, on behalf of the Society, to make the Presentation of the Longstaff Medal, which has been awarded to you by the Council in recognition of your long-continued, faithful, and brilliant services to Chemical Science.

"Your numerous and remarkable researches on the inactivity of dry gases which culminated in the wonderful discovery that carefully dried oxygen and hydrogen can be heated to the temperature of molten silver without ex-



plosion, are of such fundamental importance that an account of them finds a place in the teaching which is imparted even to most elementary students of chemistry, whilst the explanation of your results still baffles all but those who delight in daring speculations.

"You have not, however, restricted yourself to the exploitation of this field in which your skilled labour has turned up so many treasures; but, undaunted by the failure of others, you have directed your attention to the study of the eccentric element tellurium, and have embarked with your great experimental resources on an inquiry into the much-discussed question of its purity. Although in this enterprise you have failed to convict tellurium of being contaminated by any subtle attachment, for you have not shaken the accepted atomic weight of this element, yet the undertaking was distinguished by the care, the skill, and the thoroughness which we have learnt to associate with all your work.

"In handing you this medal I would take the opportunity of offering you my personal congratulations, as well as those of the Society, on your recent appointment to the Chair of Chemistry in the Imperial College of Science and Technology, and I would express the earnest hope that you may there, as the successor to Sir William Tilden and to Sir Edward Thorpe, find a congenial atmosphere in which to further prosecute your important researches."

The PRESIDENT then delivered his Address, entitled, "Some Stereochemical Problems." Prof. R. MELDOLA proposed a vote of thanks to the President, coupled with the request that he would allow his Address to be printed in the *Transactions*. The motion was seconded by Prof. J. J. DOBBIE, and carried with acclamation, the PRESIDENT making acknowledgment.

The Report of the Scrutators was presented, and the PRESIDENT declared that the following had been elected as Officers and Council for the ensuing year:—

*President*—Percy F. Frankland, Ph.D., LL.D., F.R.S.  
*Vice-Presidents who have filled the office of President*—  
—H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, O.M., D.Sc., F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; Harold B. Dixon, M.A., Ph.D., F.R.S.; A. G. Vernon Harcourt, M.A., D.C.L., F.R.S.; R. Meldola, D.Sc., LL.D., F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; William Odling, M.A., M.B., F.R.S.; Sir William Ramsay, K.C.B., LL.D., F.R.S.; J. Emerson Reynolds, Sc.D., M.D., F.R.S.; The Rt. Hon. Sir Henry E. Roscoe, LL.D., F.R.S.; Sir Edward Thorpe, C.B., LL.D., F.R.S.; Sir William A. Tilden, D.Sc., F.R.S.  
*Vice-Presidents*—G. T. Beilby, LL.D., F.R.S.; M. O. Forster, D.Sc., Ph.D., F.R.S.; A. Liversidge, LL.D., F.R.S.; E. J. Mills, D.Sc., LL.D., F.R.S.; G. T. Morgan, D.Sc.; W. J. Pope, M.A., F.R.S.

*Treasurer*—Alexander Scott, M.A., D.Sc., F.R.S.  
*Secretaries*—Arthur W. Crossley, D.Sc., Ph.D., F.R.S.; S. Smiles, D.Sc.

*Foreign Secretary*—Horace T. Brown, LL.D., F.R.S.  
*Ordinary Members of Council*—W. A. Bone, D.Sc., Ph.D., F.R.S.; W. R. Bousfield, M.A., K.C.; Adrian J. Brown, M.Sc., F.R.S.; H. G. Colman, D.Sc., Ph.D.; A. Harden, D.Sc. Ph.D., F.R.S.; A. R. Ling; T. M. Lowry, D.Sc.; A. McKenzie, D.Sc., Ph.D.; H. Marshall, D.Sc., F.R.S.; J. C. Philip, D.Sc., Ph.D.; Sir Boverton Redwood, Bart., D.Sc.; E. J. Russell, D.Sc.

**Halogen Derivatives of Phenolic Oxides.**—A. Mailhe and M. Murat.—The oxides of phenyl and cresyl can easily be obtained by Sabatier and Mailhe's method, using thoria as a catalyser. Chlorine and bromine replace the atoms of hydrogen in these phenolic oxides, giving first a derivative which contains one halogen atom in the nucleus, and then a dihalogen derivative in which one halogen atom is present in each nucleus. These compounds are relatively stable, and some of them react with magnesium. —*Comptes Rendus*, cliv., No. 9.

## NOTICES OF BOOKS.

*Micropetrology for Beginners.* By J. E. WYNFIELD RHODES, B.Sc. (Hons) Lond. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1912. (2s. 6d. net).

CANDIDATES for examinations in Geology at London University have reason to be grateful to the author of this work, for he has provided them with an excellent introduction to the study of more advanced works on Petrology such as has long been wanted by beginners and elementary students. It describes the use of the petrological microscope and the general optical properties of minerals, and gives detailed accounts of a typical series of sections which the student is advised either to prepare or obtain and thoroughly study under the microscope. A very useful synopsis of the igneous rocks, showing the relationships of the different types to one another, will be appreciated by examination candidates, as well as the glossary and the short account of more advanced methods of identifying minerals.

*Outlines of General Chemistry.* By WILHELM OSTWALD. Translated with the Author's sanction by W. W. TAYLOR, M.A., D.Sc. Third Edition. London: Macmillan and Co., Ltd. 1912. (17s. net).

THE third English edition of Prof. Ostwald's "Treatise on General Chemistry" has been prepared from the fourth German edition, which had undergone thorough revision at the hands of the author. This revision involved a good deal more alteration than was necessary simply to bring the text up to date by the addition of fresh matter describing recent discoveries and advances. Prof. Ostwald, recognising that the original was a book which was very difficult for the student to master, endeavoured to alter it in such a way as to make it easier and more readable, and succeeded admirably. At the same time he made extensive additions to the text, adding new chapters on ions in gases and radioactivity, and on the chemistry of colloids or microchemistry, and very considerably enlarging Book III., on Chemical Kinetics and Equilibrium, and Book IV., on Electrochemistry. The translation carefully reproduces the author's meaning, though the diction is not always above reproach on the score of clumsiness, and it is surprising to find that a glaring misprint has been passed over at the very beginning of the book.

*A College Text-book of Physics.* By ARTHUR L. KIMBALL, Ph.D. London: G. Bell and Sons, Ltd. New York: Henry Holt and Co. 1912. (10s. 6d. net).

THIS book has been written specially for those students of science who wish to obtain a general knowledge of the phenomena of Light, Sound, Heat, Electricity, &c., without going deeply into the mathematical aspects of the subject. The author has undoubtedly the gift of explaining his meaning in very simple language, which may be relied upon to give his readers ideas which are accurate as far as they go, and, moreover, are quite definite and precise. The arrangement of the text is thoroughly satisfactory, and although the first part is perhaps necessarily less interesting than the later sections the average non-mathematical student should be by no means unduly repelled by the treatment of Mechanics and the Properties of Matter, which form the introduction to Wave Motion and Sound. Heat follows, then Magnetism, Electrostatics, Electric Currents, Radio-activity, and, lastly, Light. Sets of problems for solution are given at various stages of the book; they are mostly quite easy, and in those cases in which they are a little more intricate answers are appended.

*Portland Cement.* By RICHARD K. MEADE, M.S. Second Edition. Easton, Pa.: The Chemical Publishing Co. London: Williams and Norgate. 1911.

IN the recently issued second edition of this work the section on the manufacture of cement has been very much enlarged, and descriptions of all modern appliances and processes have been added. Although more attention is paid to American methods, English and German practice are by no means entirely neglected, and the section gives a very good idea of the present state of the cement industry. A new chapter on the Investigation of Materials for the Manufacture of Portland Cement has been added. It discusses shortly questions of prospecting and methods of conducting trial borings. The section on Physical Testing has also been somewhat extended, and details of recent standard specifications and methods of testing have been added.

*An Introduction to Practical Chemistry.* By G. B. NEAVE, M.A., D.Sc., and J. WATSON AGNEW, F.I.C. London, Glasgow, and Bombay: Blackie and Son, Ltd. 1911.

THIS book contains a course of simple experiments in practical chemistry, and might well be used as a laboratory guide by a student who was attending lectures for beginners in the science. The preparation of various gaseous elements, acids, and salts is described, and a certain amount of elementary quantitative work is introduced. The experimental details are given very fully, and possibly too little is left to the ingenuity and powers of observation of the student, who is not only told all he is to do, but also all he is to see, as well as the conclusions to be drawn. Some rather unusual experiments for an elementary course are inserted and very carefully described. These include the determination of the composition of ammonia by means of sodium hypobromite, and some other fairly easy experimental determinations of composition.

*J. H. van't Hoff's Amsterdamer Periode, 1877—1895.* ("J. H. van't Hoff's Amsterdam Period, 1877—1895"). By Dr. W. P. JORISSEN and Dr. L. TH. REICHER. Helder (Holland): C. de Boer, jun. 1912.

THE authors of this monograph on van't Hoff were intimately acquainted with him during his residence in Amsterdam, and are well qualified to write an appreciation of the important work he did while there. Before van't Hoff's own discoveries are discussed some account of his predecessors at the Athenæum is given, and of the state of chemical teaching in Amsterdam, and then the authors describe vividly the conditions under which he worked in the laboratory, and the stimulating effect of his personality upon his students and assistants. The book contains four discourses of van't Hoff's, translated into German, and is a fitting tribute to the memory of the great chemist.

*Onoranze Centenarie Internazionali ad Amedeo Avogadro.* ("International Celebrations of the Centenary of Amedeo Avogadro"). Turin: Unione Tipografica - Editrice Torinese. 1911.

THE year 1911 was the hundredth anniversary of the publication by Amedeo Avogadro of the famous memoir in which his hypothesis concerning the molecular volume of gases was first put forward, and the occasion was suitably celebrated at Turin, which was his native place. It is not too much to say that Avogadro's hypothesis was one of the most important contributions that has ever been made to the theory of chemistry, and the chemists of all nations united to do honour to his memory. The volume issued in commemoration of the occasion contains photographs of the great chemist and of the statue raised to him in Turin, with full descriptions of the festivities which took

place in September, and reproductions of the discourses delivered by Prof. Guareschi and others. An interesting fac-simile of the first page of the famous memoir is included.

*Helix Chemica.* By B. K. EMERSON.

THIS study of the periodic relations of the elements and their graphic representation is reprinted from the February, 1911, number of the *American Chemical Journal*. It should be read by all who are interested in the question of the evolution of the elements; the helix described in it was devised by the author after he had discussed the subject with Prof. Hopkins and studied the latter's valence-volume curve. The paper is excellently illustrated by figures and diagrams, and the predictions based upon the helix are particularly interesting.

*Anwendung Physikalisch-chemischer Theorien auf Technische Prozesse und Fabrikationsmethoden.* ("Application of Physico-chemical Theories to Technical Processes and Methods of Manufacture"). By Prof. ROBERT KREMANN. Halle-a-S.: Wilhelm Knapp. 1911.

THE author of this work has found that in his experience chemical students take a very great interest in those problems of physical chemistry which are most closely connected with technical processes, and he has been in the habit of delivering to his students a course of special lectures on the Application of Physico-chemical Theories to technical problems. These lectures are reproduced with some amplifications in this volume of the "Monographien über Chemisch-technische Fabrikationsmethoden." The book aims at giving a general and broad view of the subject, rather entering into full details. It opens with a discussion of the two laws of thermodynamics and their applications to reduction and oxidation processes of technical importance. Chapter II. deals with the velocity of reactions and catalysers, and in it the lead chamber process, the catalysing action of colloidal platinum and of ferments are lucidly treated. In subsequent chapters the law of mass action and the Phase Law are considered in some detail, and although the student would find the book by no means easy to read it is certainly a mine of information, and he would learn from it to regard technical questions from a thoroughly scientific point of view.

*Notice sur les Travaux et Titres Scientifiques de M. Charles Moureu.* ("Notice of the Scientific Work and Distinctions of M. Charles Moureu"). Paris: A. Davy. 1911.

THIS book opens with a general review of all the original work which has been published by Prof. Charles Moureu, and many of his papers are reprinted almost in full. His work has lain chiefly in the region of organic chemistry, where possibly his most important results have been obtained in the preparation of synthetic products and naturally occurring substances of vegetable origin. His work on acrylic acid and its derivatives and upon the acetylenic compounds has led to the discovery of many general reactions for preparing various organic substances, and he was the first to prepare carbon subnitride,  $C_4N_2$ , and cyan-acetylene,  $C_3NH$ . He subjected the alkaloid spartein to a particularly exhaustive examination and elucidated its nature, and in addition has done a considerable amount of valuable work in spectroscopy and in the investigation of the gases of thermal springs and the inert gases. The book contains a complete chronological list of all Prof. Charles Moureu's works, and also of the lectures he has delivered before the learned societies and the articles published by him in the scientific journals.



*La Pila Elettrica.* ("The Electric Cell"). By A. ASTOLFONI. Milan: Urico Hoepli. 1912. (3 L.).

THIS book is written for people of limited scientific knowledge, and aims at giving them practical and useful information regarding the structure and uses of the electric cell. The first three chapters are devoted to the general theory of the cell, and methods of taking measurements of resistance, E.M.F., &c. Unnecessary details are avoided, and many illustrations and diagrams explain the text. The principal types of cells, both dry and wet, are then described, and while more attention is paid to those which are most widely employed, others of historical or theoretical interest are not entirely passed over. The last chapters give short accounts of the nature and the properties of all substances which are used in making electric cells.

*Uebungsbeispiele für die Elektrolytische Darstellung Chemischer Präparate.* ("Practical Examples of Electrolytic Methods of Preparing Chemical Substances"). By Dr. KARL ELBS. Second Edition. Halle-a.-S.: Wilhelm Knapp. 1911. (5 Mk. 40).

THIS is undoubtedly a book that was really wanted, and its author is to be congratulated upon having produced a useful, compact, and yet complete treatise on the preparative side of electrochemistry. It contains some general directions for electrolytic work, but is not intended for the use of those who have had no experience whatever in practical electricity. On the other hand, it gives full details of methods of preparing a great number of substances, both organic and inorganic, and many references to the original papers in which their preparation was first described. The second edition contains some new examples of methods of electrolytic preparation, and various minor alterations and improvements have been made in the text.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. cliv., No. 9, February 26, 1912.

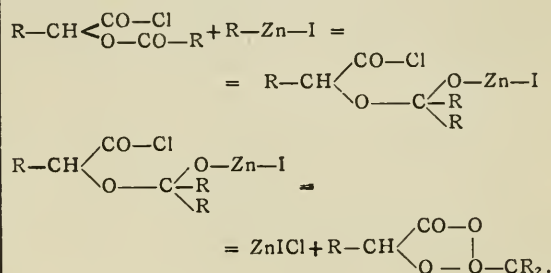
**Preparation of 1.5-Diphenyl and 1-Phenyl-2.2.4.4-tetramethyl-3-pentanone.**—A. Haller.—The action of sodamide and methyl iodide on symmetrical dibenzylacetone gives tetramethyldibenzylacetone or 1.5-diphenyl-2.2.4.4-tetramethyl-3-pentanone. 1-Phenyl-3-pentanone can be methylated similarly, but benzylacetone simply condenses when treated with sodamide and methyl iodide, and does not yield benzylidimethylpinacolone. These researches show that the diaryl and monoarylketones of types  $\text{ArCH}_2\text{CH}_2\text{COCH}_2\text{CH}_2\text{Ar}$  and  $\text{ArCH}_2\text{CH}_2\text{COCH}_2\text{CH}_2\text{Al}$  can be tetramethylated in the same way as the dialkyl ketones, and the new ketones are split up like the trialkylacetophenones and the hexalkylketones.

**New Catalytic Method of Preparing Aldehydes from Acids.**—Paul Sabatier and A. Mailhe.—By passing a mixture of formic acid and another acid of the formic acid series over titanic oxide heated to 250° to 300° the latter acid can be converted into the corresponding aldehyde. The yield varies from 40 per cent with propionic acid to 90 per cent with octylic acid. Thoria can be substituted for titanic oxide if the temperature is kept between 270° and 300°. The yields range from 25 or 30 per cent to 65 per cent in the case of isobutylic acid.

**Permeability of Iron for Hydrogen.**—G. Charpy and S. Bonnerot.—For a mixture of gases containing hydrogen

iron appears to be a true semi-permeable membrane. The phenomenon in the cold with nascent hydrogen is very different from that at higher temperatures, being irreversible. The different quantitative results obtained seem to agree with the hypothesis of the formation of a solution of hydrogen in the iron.

**Synthesis by means of Mixed Organometallic Derivatives of Zinc.**—E. E. Blaise.—The mixed zinc organo-derivatives would normally react with acid chlorides to give the ethers of  $\alpha$ -ketone alcohols, but as a matter of fact the product of the reaction is a closed-chain compound. Apparently the reactions are—



The author suggests the name "mixed cycloacetals" for these products, many examples of which he has prepared.

**Oxyhydrofuranes.**—Georges Dupont.—Tetramethyloxyhydrofurane and dimethyldiethyl-oxyhydrofurane may be prepared by hydrogenating the corresponding ketohydrofuranes with sodium and alcohol. Organo-magnesium compounds act upon derivatives of  $\alpha\alpha'$ -dimethyl-ketohydrofurane to give the derivatives of oxyhydrofurane. With derivatives of tetramethyl-ketofurane hydrocarbon is set free, but the bromides of methyl, acetylene, and benzylmagnesium yield oxyhydrofuranes.

Vol. cliv., No. 10, March 4, 1912.

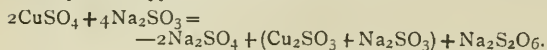
**Complex Ferric Compounds. Ferric Fluoride.**—A. Recoura.—When ferric fluoride is dissolved only a third part of the fluorine takes part in double decompositions. The composition of the fluoride is expressed by the formula  $\text{FeF}_4(\text{OH})_2(\text{HF})_2 + 4\text{H}_2\text{O}$ . When the solid salt is heated it first loses fluorine, the loss being proportional to the time, for the first third of the fluorine. Afterwards the loss becomes extremely slow. The loss of water is very rapid at first, and then becomes regular and strictly proportional to the loss of fluorine, until a third of the latter has passed off. The salt undergoes no further loss at 95°. The explanation of these facts is as follows:—Firstly, the fraction of the  $4\text{H}_2\text{O}$  of crystallisation, which can be driven off at 95°, is rapidly removed; secondly, the fluoride decomposes according to the equation  $\text{FeF}_4(\text{OH})_2(\text{HF})_2 = 2\text{HF} + \text{H}_2\text{O} + \text{Fe}_2\text{F}_4\text{O}$ . This second phenomenon is at first masked by the first.

No. 11, March 11, 1912.

**Refraction and Dispersion of Mercury Nitrates.**—P. Th. Muller and E. Carrière. From determinations of the dispersion and molecular refraction of the nitrates of mercury it appears that the refraction of the bivalent atom of mercury is decidedly greater in the organo-metallic compounds than in mercuric nitrate. The refraction and dispersion of the atom of mercury in the complex  $\text{Hg}_2$  (mercurous nitrate) are much greater than those of the same atom in the state of a simple ion (mercuric nitrate).

**Formation of Dithionic Acid in the Action of Alkaline Sulphites on Salts of Copper.**—H. Baubigny.—When sodium sulphite acts on copper sulphate crystals of a double sulphite of soda and cuprous oxide are obtained, and dithionic acid is formed. The formation of this latter acid is a phenomenon of the same order as that

which takes place with the salts of silver, but with copper salts the reaction takes place more quickly in the cold. The equation appears to be—



In two determinations of the amount of dithionic acid the yield was found to be 57.9 and 69.4 per cent respectively of the theoretical yield calculated from this equation.

**Apo-harminecarbonic Acid, Apo-harmine, and some Derivatives.**—V. Hasenfratz.—The author has devised an apparatus by means of which large quantities of apo-harmine can be obtained by the distillation of harmic acid,  $\text{C}_{10}\text{H}_8\text{N}_2\text{O}_4$ . The decomposition of the acid takes place in two stages; between  $250^\circ$  and  $280^\circ$  one molecule of  $\text{CO}_2$  is eliminated, the product being apo-harminecarbonic acid,  $\text{C}_8\text{H}_7\text{N}_2(\text{CO}_2\text{H})$ . This acid loses  $\text{CO}_2$  at  $330^\circ$  and gives apo-harmine. When an aqueous solution of apo-harmine containing potash is treated with iodine dissolved in potassium iodide, iodoapo-harmine,  $\text{C}_8\text{H}_7\text{IN}_2$ , is deposited. It unites with methyl iodide to give iodohydrate of methyl-iodoapo-harmine. Apo-harminesulphonic acid can be obtained by dissolving apo-harmine in cold concentrated sulphuric acid. Probably the two carboxyls of harmic acid are in the  $\alpha$ - and  $\beta$ -positions with regard to one of the nitrogen atoms of apo-harmine. Thus harmic acid is  $\alpha$ - $\beta$ -apo-harminecarbonic acid, and at  $250$ – $280^\circ$  it decomposes into the  $\beta$  acid, losing the carboxyl from the  $\alpha$ -position.

**$\gamma$ -Ethoxyacetylacetic Ether.**—Marcel Sommelet.—Ethoxyacetic ether and bromoacetic ether react in presence of zinc to give a zinc complex, which is decomposed into  $\gamma$ -ethoxyacetylacetic ether by means of water. The ether gives a cuprous compound,  $(\text{C}_2\text{H}_5\text{O}.\text{CH}_2.\text{CO}.\text{CH}=\text{CO}_2\text{C}_2\text{H}_5)_2\text{Cu}$ , with cupric acetate solution. When it is heated with an alcoholic solution of hydrazine hydrate ethoxymethyl-3-pyrazolone is formed.

**Action of Phenyl Magnesium Bromide on Pinacolone and Methylpinacolone.**—Mdme. Ramart-Lucas.—Phenyl magnesium bromide reacts with pinacolone to give 2,2-dimethyl-3-phenyl-3-butanol, and with methylpinacolone the corresponding pentanol is obtained. Hence the products of the action of alkyl magnesium iodides on trimethylacetophenone, and of phenyl magnesium bromide on pinacolone and methylpinacolone, are identical.

**1-ol-4-Pentene.**—H. Pariselle.—1-ol-4-pentene may be prepared by allowing allyl bromide to drop on to magnesium and adding aldehyde when the action begins to slacken. Finally sulphuric acid is added, and the aqueous solution is extracted with ether. The ethereal solution is distilled, and the fraction passing over between  $100^\circ$  and  $130^\circ$  on rectification yields the required alcohol. The author has prepared its acetic and hydrochloric ethers, and from the latter has obtained 2,4-dichloropentane by the fixation of hydrochloric acid.

**Action of Caustic Potash on Tertiary Alcohols—New Method of Diagnosing Alcohols.**—Marcel Guerbet.—The primary, secondary, and tertiary alcohols behave differently with caustic potash, and with alcohols of high molecular weight the following method may be used to determine to which class a given alcohol belongs. The alcohol is heated in a sealed tube for sixteen hours to  $230^\circ$  with previously dehydrated caustic potash. After cooling the tube is opened under water. If the alcohol is primary or secondary a considerable volume of gas is disengaged, while if it is tertiary very little or no gas is evolved. Water is then poured on the contents of the tube. If the alcohol is primary the whole is dissolved, while if it is tertiary an oily layer is formed on the top of the aqueous solution.

**Nitroderivatives of Oxide of Phenyl.**—A. Mailhe and M. Murat.—By the direct action of nitric acid the nitroderivatives of oxide of phenyl can be obtained. The mono-nitro compound has to be prepared in an acetic medium.

The highest nitro-derivative thus obtained in the hexanitratated compound. All the compounds are readily reduced to the corresponding amines.

## MISCELLANEOUS.

The University of Leeds.—*New Livesey Professor of Coal-gas and Fuel Industries.*—On the recommendation of the Livesey Memorial Committee, the University Council have appointed Mr. John William Cobb, B.Sc., to be Livesey Professor of Coal-gas and Fuel Industries from the end of the present academic year, when the Chair will be vacated by Dr. W. A. Bone, F.R.S., who has accepted the Professorship of Fuel and Refractory Materials at the Imperial College of Science and Technology. Professor Cobb, who was born in 1873, received his early education at the Leeds Modern School, and is a former Scholar and Prizeman of the University of Leeds and Exhibitioner and B.Sc. of the University of London. Since 1891 he has been engaged with the Farnley Iron Company, in the first instance as Chemist, and more recently as Technical Assistant to the Managing Director, Mr. R. Armitage, M.P. The control and development of fuel-using processes at the works of the Farnley Iron Company have been largely under Mr. Cobb's control, especially since the introduction of the Mond gas process with ammonia recovery, of which the Farnley Iron Company was one of the first users. The gas has been brought into service for furnace heating, and for burning glazed ware, as also for power through gas-engines. Professor Cobb has made many contributions to scientific journals, mainly of a technical character, concerning coal, the working of furnaces, the testing of clay-ware, the constitution and synthesis of glazes, and the corrosion of iron.

## MEETINGS FOR THE WEEK.

- MONDAY, 6th.—Royal Society of Arts, 8. (Howard Lecture). "Heavy Oil Engines," by Capt. H. R. Sankey, R.E.  
— Royal Institution, 5. General Meeting.  
— Society of Chemical Industry, 8. "New Apparatus for the Coking Tests of Coal," by R. Lessing. "New Method for the Determination of Ferrocyanides," by H. E. Williams. "A Drying Oven," by J. H. Coste. "Indiarubber as a Protective Colloid," by E. W. Lewis and H. Waumsley.
- TUESDAY, 7th.—Royal Institution, 3. "Insect Distribution, with special reference to the British Islands," by F. Balfour Browne, M.A.  
— Royal Society of Arts, 4.30. "Colonial Vine Culture," by Alan Burgoyne.
- WEDNESDAY, 8th.—Royal Society of Arts, 8. "British Rule in Nigeria," by E. D. Morel.
- THURSDAY, 9th.—Royal Institution, 3. "Recent Explorations in the Canadian Rocky Mountains," by Prof. J. Norman Collie, F.R.S., &c.  
— Royal Society, "Variation with Temperature of the Rate of a Chemical Change," by A. Vernon Harcourt. "Some Phenomena of Sun-spots and of Terrestrial Magnetism," by C. Chree. "The Ultimate Lines and the Quantities of the Elements producing the Lines in Spectra of the Oxy-hydrogen Flame and Spark," by Sir W. N. Hartley. "Transformations of the Active Deposit of Thorium," by E. Marsden and C. G. Darwin. "The  $\beta$ -Particles reflected by Sheets of Matter of different Thicknesses," by W. Wilson.
- FRIDAY, 10th.—Royal Institution, 9. "The Gaumont Speaking Cinematograph Films," by Prof. A. Stirling, M.D.  
— Physical, 8. "Method of Measuring Small Inductances," by S. Butterworth. "Conversion of Starch into Dextrin by X-rays," by H. A. Colwell and S. Russ. "Apparatus for Showing the Generation of Electricity by Carbon at High Temperatures," by J. A. Harker and G. W. C. Kaye. "Calibration of Wave-meters for Radio-telegraphy," by G. W. O. Howe.
- SATURDAY, 11th.—Royal Institution, 3. "Interpretation in Song," by H. Plankett Greene.



# THE CHEMICAL NEWS.

VOL. CV., No. 2737.

## A WATER-SEALED CONSTANT-PRESSURE HYDROGEN GAS GENERATOR.\*

By S. H. COLLINS.

In some work on the rate of evolution of hydrocyanic acid it became necessary to generate pure hydrogen at a steady rate of 10 litres per hour. Many forms of apparatus were employed, with the result that a new system was perfected.

The chief advantages of the apparatus here described are that :—

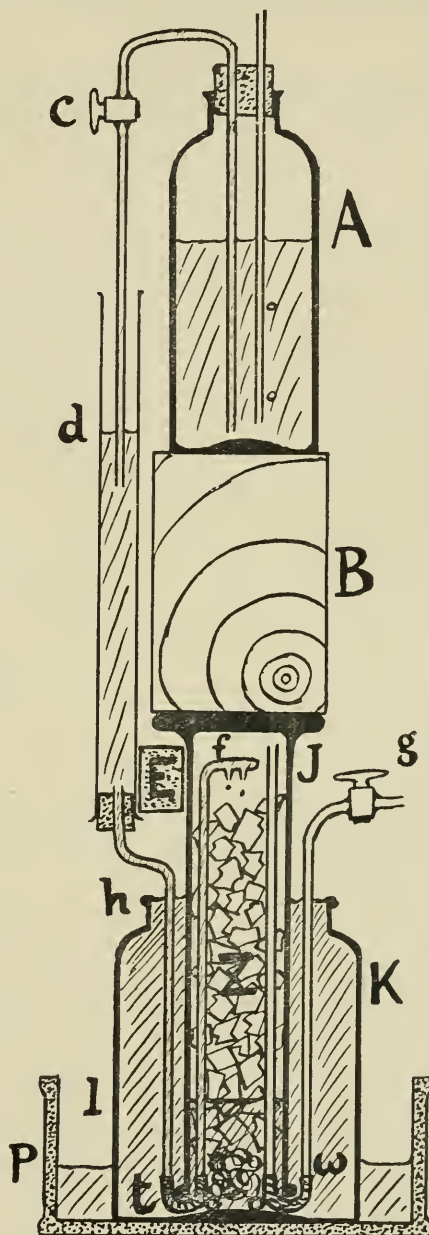
1. The pressure of the gas can be easily varied over a wide range.
2. Air cannot possibly diffuse in through rubber connections, &c.
3. The zinc need not be granulated, but only broken into lumps.
4. Economy of acid.
5. Simplicity, unbreakability, and compactness.

In the accompanying figure A is a Winchester quart bottle delivering dilute sulphuric acid ( $1:8$  by volume) at constant level  $d$ ,  $c$  is a tap for shutting off acid at night. The wooden block B provides the coarse adjustment, the air tube in A provides the fine adjustment for pressure of gas. The wide tube D is roughly graduated in centimetres, counting the level of the sprinkler  $f$  as zero. The working pressure of gas reckoned in terms of a column of dilute sulphuric acid can be seen at any time. The cork block E fastens the tube  $d$  to the inverted cylindrical jar J, two or three turns of copper wire making the connection a semi-rigid one. The large glass bottle K serves to hold the waste acid, and also, in conjunction with the jar J, serves as a gas-holder to maintain regularity of gas supply. The pneumatic trough P receives the waste acid after it has done duty. From time to time the trough is emptied by syphon or otherwise. The lumps of zinc are represented by  $z$ , which rest upon a ball made by tangling some copper wire. Between the mouth of the jar J and the bottom of the bottle K are two pieces of wide rubber tube to form a cushion and prevent breakage. It is convenient to attach these pieces permanently to the jar J by a copper wire. The acid supply tube has a rubber connection at  $t$ , and the gas-delivery tube has a similar rubber tube at  $w$ . These rubber tubes should be much narrower than the tubes used as a cushion for J, otherwise the weight of the zinc and acid might close them. The height from  $l$  to  $h$  measures the pressure of the gas in terms of saturated zinc sulphate solution, hence  $HL$  is only about  $\frac{1}{3}$   $df$ . Three corks are hammered into the mouth of K to fix J firmly. Evaporation takes place in P, causing zinc sulphate to crystallise out and firmly cement K to P. A little hot water will at any time remove this zinc sulphate if required. The zinc and the trough are heavy and bring the centre of gravity of the whole apparatus low down, thus providing stability.

It is convenient to have the bottle A in duplicate with rough marks at 2000 cc. and 2300 cc. Water up to the 2000 mark is put into the spare bottle, strong sulphuric acid poured to the 2300 mark, and the fresh bottle of acid put up in place of the bottle which has become exhausted without causing any interference with the flow of gas. The jar J holds about 7 kilograms of zinc and only needs recharging at long intervals. For recharging, A and B are lifted off, the three corks in the mouth of K removed, and the jar J slowly lifted. When the bulk of the waste liquid

has drained off, the jar J is stood on its proper foot with the tube  $d$  hanging below the level of the table. The copper wire ball is removed and the zinc poured in.

The hydrogen obtained was quite free from oxygen, but contained sulphuretted hydrogen, arseniuretted hydrogen, and perhaps phosphuretted hydrogen and acetylene. Bubbling a gas through liquids renders pressure control



very difficult, and rubber connections were undesirable. To get over the difficulty a new absorbing agent was used. If about 3 parts of powdered mercuric chloride and 1 part of lime be mixed, made into a paste with water, dried, broken up, sieved, and the convenient sized lumps bottled, a very fine absorbent for all the impurities can be obtained. This "mercury lime" needs only one tube and therefore

\* Read before the University of Durham Philosophical Society, November 24th, 1911.

few connections, works rapidly, and shows the progress of the absorption of impurities by turning first yellow, then black.

(We are indebted to the Author for the woodcut illustrating this Paper).

## LABORATORY PREPARATION OF LITMUS-PAPER.

By E. W. RICE.

EXPERIENCE has shown that with a good quality of litmus-paper, uneducated workmen are able to distinguish slight differences in shade, and maintain very slight acidities or alkalinities, if such are desired. It is found, however, that they are often deceived by the quality of the litmus-paper, which, through varying amounts of salts in the paper, may require widely differing amounts of acid or alkali to give a definite colour.

Practically all directions for the laboratory preparation of litmus-paper start with commercial litmus, and require from 10 per cent to 33 per cent solutions to make a sufficiently coloured paper. Various methods of purifying this commercial product before its use may be found in the literature, all of which require considerable time for sedimentation, and, usually, quite an amount of alcohol, which makes purification expensive. A great many have used a water extract of commercial litmus without further purification, neutralising to meet their requirements. This gives a paper which is satisfactory for some purposes, but the red paper is usually rather impervious to water, and the large amounts of soluble salts which it contains cause reactions in the paper which are often deceiving.

These various difficulties have led to the use of the chemically pure litmus which is sold by the various supply houses and can be prepared in about one-quarter of the time required by the ordinary substance. Although the chemically pure litmus is listed at ten times the value of the commercial product, its colouring strength is so much greater that the final cost is never more, and in some cases is less. Continued trials have shown the following to be a very satisfactory grade of litmus-paper for all purposes, whether laboratory or manufacturing, and the product will be found more delicate than most litmus-papers on the market.

For blue paper, 1.4 per cent of chemically pure litmus is dissolved in distilled water with constant shaking for about one hour. This solution is set aside over night, carefully decanted from the small amount of sediment, and sulphuric acid added, drop by drop, sufficient to reduce alkalinity to such a point that a piece of filter-paper floated on the top and then dried will assume a very perceptible red colour after being suspended one half minute in  $N/2000$  hydrochloric acid.

To make red litmus-paper a 1.0 per cent solution of chemically pure litmus is required with the addition of sulphuric acid until such a degree of acidity is reached that a very perceptible reaction will take place when paper floated and dried as before is suspended one-half minute in  $N/4000$  caustic soda solution.

Time of exposure to these standardising solutions is found to be as important a function as the degree of acidity or alkalinity of the paper. The above-mentioned degrees of sensitiveness are close to the practical limits, for if the papers are made more delicate they cease to be red and blue, but become lilac or neutral.

The filter-paper used is any smooth compact qualitative paper sold by the chemical supply houses. The best manner to saturate the paper with litmus has been found to cut it in strips about 7 inches wide, and to draw the paper over the surface of the litmus solution, which has previously been placed in an ordinary shallow square-cornered enamelled bread-baking pan. The paper is held by the ends and first touched to the surface of the liquid, about 2 inches from one end; then the other end is re-

leased and the paper drawn down across the edge of the pan. Surface tension holds the paper to the liquid, yet only one side of the paper is allowed to touch the solution, and drawing across the side of the pan takes away any excess. The strips are hung up to dry by pinning the blank ends over lines stretched in some convenient place.

The paper will be found very uniform, as just sufficient solution will have been taken up to dye all the sheets of the same shade. One litre of solution will make one hundred sheets 7 inches by 20 inches in size.

These sheets may be rolled up or packed away in proper containers to protect them from the air, and cut in strips of convenient size for use shortly before they are needed. Wide-mouthed glass-stoppered bottles are found very convenient for holding the small strips for daily use. Great uniformity is secured by making up large batches at a time, and the method allows for closest similarity of succeeding batches.—*Journal of Industrial and Engineering Chemistry*, iv., No. 3.

## THE EFFECT OF ORGANIC AND INORGANIC "ADDITION AGENTS" UPON THE ELECTRO-DEPOSITION OF COPPER FROM ELECTROLYTES CONTAINING ARSENIC.\*

By CHING YU WEN and EDWARD F. KERN.

In the electrolytic process for the refining of copper many of the impurities, notably arsenic and antimony, accumulate in the electrolyte, from which they may be subsequently deposited upon the cathode, causing the cathode copper to be nodular and brittle. Arsenic, as has been well known, may accumulate up to a certain more or less definite concentration before it begins to contaminate the deposited copper. In practice, then, it is of primary importance to keep the electrolyte up to a certain degree of purity, which is usually accomplished by withdrawing portions of the electrolyte at intervals, and replacing it with fresh solution, the copper being recovered from the impure solution by crystallisation, or by electrolysis, using insoluble anodes. This frequent replacement of electrolyte, and the corresponding recovery of copper from the impure solution, complicates the process of refining and adds to its cost.

The formation of dendritic "trees," particularly upon the edges of the cathodes, is a source of trouble and expense to the refiner, for these "trees" must be removed by hand labour lest they short-circuit the current.

The investigation here reviewed was carried out with the two-fold object:—

"First, to prevent the deposition of arsenic and antimony upon the cathode, and, second, to prevent the formation of dendritic 'trees.'"

The problem was to produce solid and smooth deposits from copper electrolytes high in arsenic by the aid of organic and inorganic "addition agents."

The literature shows that little investigation of "addition agents" has been made in the past. The authors review the work done upon the subject, notably that of Kiliani (*Berg und Hüttenmännisches Zeitung*, 1885, p. 249), Borchers ("Electrolytic Smelting and Refining," p. 206), Hoffman (*T.A.I.M.E.*, 1904, xxxiv., 312), Wicks ("Thesis," School of Mines, Columbia Univ.), Kern and Jarves (*School of Mines Quarterly*, 1909, xxx., 119) and Förster and Seidel (*Zeit. f. Electrochem.*, 1899, v., 508). Their results may be summarised as follows:—The per cent of arsenic deposited from solution is not a function of the potential difference between electrodes ("Thesis," School of Mines, Columbia Univ.). "The function of an

\* A review of a Paper presented at the Twentieth General Meeting of the American Electrochemical Society in Toronto, Canada. From the *Chemical Engineer*, xiv., No. 6.



addition agent in an electrolyte is to maintain a reducing menstuum around the cathode, which, in turn, causes the deposit to form denser and smoother" (*School of Mines Quarterly*, 1909, xxx., 119). The deposits formed in electrolytes containing alkali or alkaline earth salts are generally smoother and less crystalline than those from electrolytes which do not contain those salts, the explanatory theory being that the good deposit is due to the reducing effect of the alkali or alkaline earth metal ions surrounding the cathode (*Trans. Am. Electrochem. Soc.*, 1909, xv., 472). The deposits formed at higher temperatures are more coarsely crystalline, and show a higher tensile strength than those formed at lower temperatures (*Zeit. f. Electrochem.*, 1899, v., 508).

The materials used in the various series of experiments were as follows:—

Copper anodes,  $4\frac{1}{2}'' \times 2\frac{3}{4}'' \times \frac{3}{8}''$ , containing about 1 per cent As and 1 per cent Sb.

Pure sheet copper cathodes.

Electrolytes:—A, 15 per cent  $\text{CoSO}_4$ ,  $\text{SH}_2\text{O}$ , and 10 per cent  $\text{H}_2\text{SO}_4$ . B, 15 per cent  $\text{CoSO}_4$ ,  $\text{SH}_2\text{O}$ , 10 per cent  $\text{H}_2\text{SO}_4$ , and 10 per cent As as  $\text{H}_3\text{AsO}_4$ .

By mixing A and B in varying proportions, six solutions containing, respectively, 1.5, 2, 3, 4, 6, and 8 per cent As were prepared.

The apparatus consisted in a battery of eight cells, four in each of two water batteries kept at different temperatures, the space between the electrodes and the current density (40 ampères per sq. ft.) being kept constant in all experiments. Circulation of electrolyte was provided by mechanical stirrers. Most of the runs were of fifty to one hundred hours' duration, the potential between electrodes being measured at two-hour intervals.

A large number of experiments are described in detail under the following headings:—

- I. Electrolytes which contained no "addition agents."
- II. Electrolytes which contained inorganic "addition agents."
- III. Electrolytes which contained organic "addition agents."
- IV. Electrolytes which contained organic and inorganic "addition agents."

In each experiment, time, current density, potential, temperature, composition of electrolyte before and after the run, and composition of anode and cathode metal are stated, photographs of the cathodes shown, and the physical properties of the deposited copper described.

#### Summary of Experiments.

In the first series, wherein no "addition agents" were employed, four runs were made. Electrolytes containing from 1.5 to 8 per cent of As were used, and the effect of temperatures of from 20° C. to 60° C. were noted. The results point to conclusions as follows:—

When the electrolyte contains no "addition agent," large quantities of As and Sb are deposited with the copper, and large trees form on the cathode, when the percentage of As is from 1.5 to 4. When the electrolyte contains from 6 to 8 per cent of As, the As acts as "addition agent," especially at temperatures of from 40° to 60°, the deposits being purer, brighter, more dense and coherent, and less brittle than when lower percentages of As are present. In general, the deposits were better at the higher than at the lower temperatures.

In the second series, wherein inorganic "addition agents" were used, solutions containing from 1.5 to 8 per cent As were electrolysed at various temperatures and with addition of the following compounds:—NaCl (very small, and large quantities), HCl,  $\text{Na}_2\text{SO}_4$  (little and much),  $\text{Al}_2(\text{SO}_4)_3$ , and  $\text{AlCl}_3$ . Small quantities of sodium chloride, nitrate chlorate, and borate were also used as "addition agents" in electrolytes containing 1.5 per cent As, and the resulting solutions run under the same conditions.

In general, all of these salts have a good effect, both as

to purity and physical properties, upon the deposited copper, even when large quantities of arsenic are present in the electrolyte.

Of all of them, sodium chloride (present to the extent of 0.01 per cent) is best, with hydrochloric acid, cuprous and cupric chlorides, and sodium sulphate following. Aluminium sulphate has a markedly good effect as "addition agent." In general, the higher the metal of the "addition agent" in the electro-chemical series, the purer, smoother, and less brittle the deposit.

The chemical behaviour of the Na and the Cl ion in holding back the deposition of arsenic is discussed. Each shows its good effect in that all the sodium salts and all the chlorides tried improved the character of the deposit. The fact that sodium chloride is the best of inorganic "addition agents" is due to its yielding both the Na ion and Cl ion in solution.

In a third series the organic substances, gelatin, glue, tannin, and peptone were used as "addition agents," electrolytes like those used in the other experiments being employed. The first three produced a remarkably good effect upon the character of the copper deposit, both chemically and physically, while peptone has a bad influence upon the deposit.

Copper deposits formed when the electrolytes contain both organic and inorganic "addition agents" are all good. Those where the combination of gelatin and sodium chloride is used are best, while the combinations glue and sodium chloride, and glue and cuprous or cupric chloride show almost as good results upon the cathode copper. It is especially interesting that, whereas peptone alone has a very bad effect upon the copper deposit, the combination of peptone and sodium chloride makes an excellent "addition agent," the chlorine ion overcoming all the bad effects of the peptone.

In general, the higher the temperature of the electrolyte, the better the quality of the deposited copper, and, of course, the lower the resistance of the electrolyte.

The authors conclude that the combination of sodium chloride (0.01 per cent Cl) and gelatin (0.01 to 0.02 per cent) is the best "addition agent" for copper sulphate electrolytes high in arsenic, for the copper deposited under these circumstances "possesses the greatest purity and highest ductility."

#### SOME NEW FEATURES IN THE ELECTROLYTIC DETERMINATION OF LEAD.

By JOHN G. FAIRCHILD.

It has been found that good deposits of lead peroxide, free from flakes, and of close texture, can be obtained on a smooth platinum cylinder in two hours' time without rotation, and as much as 100 to 200 mgrms. in weight. This can be raised to 300 mgrms., but there is danger of flaking off. The secret of success is a low amperage to begin with and a hot solution, 50–60° C.

For alloys high in lead 2 grms. or more are weighed out, and an aliquot taken to represent about 0.1 grm. of metallic lead. The volume of electrolyte is 200 cc. in a 250 cc. beaker, and contains 30 cc. strong  $\text{HNO}_3$ . Heat to 50–60° C., using an anode of 25 sq. in. surface with a cathode cylinder of 12 sq. in. The anode should be burnished frequently, and ignited previous to placing in the electrolyte. This ignition removes any greasy film adhering to the cylinder. Split cover-glasses are used to prevent loss through evaporation of the hot solution, which just completely immerses the edge of the anode cylinder. The current is started at 0.25 am. for one hour and a-half, when it is raised to 0.5 am. for half an hour longer to remove the last traces of lead, and the cover-glasses are rinsed down. At the end of two hours deposition is complete, as shown by the newly immersed stem remaining bright. The beaker is lowered and removed, being

replaced by one containing clean water for rinsing the cylinders, which are then disconnected, the anode being rinsed in a glass of alcohol, drawn through a flame to burn off what adheres while holding the cylinder in a vertical position. It is then held for a few seconds about a foot above the flame to dry thoroughly, and weighed. On adding ammonia to the electrolyte and passing  $H_2S$ , no more than a mere brownish colour should show.

To prove the accuracy of this method, purified lead sulphate was taken as the standard. An amount equal to 0.7335 gm. was put into a 500 cc. flask, and dissolved in just enough hot am. acetate solution, 100 cc. being taken for analysis by means of a pipette standardised to the flask. After adding 30 cc.  $HNO_3$  of 1.42 sp. gr., this aliquot was made up to 200 cc. The electrolyte is best kept hot throughout the run by means of a hot plate or burner. The results for lead sulphate and test lead were as follows:—

| PbSO <sub>4</sub> . | PbO <sub>2</sub> equiv. | PbO <sub>2</sub> found. | Pb per cent (a). |
|---------------------|-------------------------|-------------------------|------------------|
| 0.1467              | 0.1157                  | 0.1156                  | 99.92            |
| 0.1467              | 0.1157                  | 0.1160                  | 100.26           |
| 0.1467              | 0.1157                  | 0.1155                  | 99.83            |
| 0.1467              | 0.1157                  | 0.1159                  | 100.17           |
| Test lead.          |                         |                         |                  |
| 0.1000              | 0.1157                  | 0.1145                  | 98.92            |
| 0.1000              | 0.1157                  | 0.1143                  | 98.72            |
| 0.1000              | 0.1157                  | 0.1142                  | 98.63            |
| 0.1000              | 0.1157                  | 0.1147                  | 99.14            |
| 0.1000              | 0.1157                  | 0.1145                  | 98.92            |
| 0.1000              | 0.1157                  | 0.1146                  | 99.04            |

(a) Conversion factor, 0.866.

Whenever a weight was low the lead was found to be not all deposited, due to faulty manipulation which is not likely to occur. If the electrodes short-circuit resolution occurs with some lead flaking off.

Lead scrap and furnace dross can be treated thus:—About 5 grms. are dissolved in  $HNO_3 + H_2SO_4$  in a Kjeldahl flask, and evaporated till fumes appear. After cooling, the impure  $PbSO_4$  is filtered off, the paper punctured, and the precipitate rinsed back into the flask. It is then treated with just sufficient hot saturated am. acetate solution, which is warmed till solution is complete, then filtered into a 500 cc. flask, a proper portion being taken for electrolysis.

On comparison with pure lead it will be seen that material relatively low in lead will require only about half-an-hour at 0.5 am., a small percentage of lead being given a higher amperage. In this way can lead be readily separated from copper, manganese, silver, antimony, &c. When a relatively large amount of copper is present, as in blister copper, only 20 cc. nitric acid may be present. The presence or absence of am. nitrate seemed to have no effect on the results.

This method gives lower results than the chromate method; thus, by the latter 59.25 per cent lead was found in a lead dross, by the electrolytic 58.85 per cent. On a copper matte high in lead, the figures gave 10.57 chromate, 10.32 electrolytic.

Material such as a copper matte can be dissolved in  $HNO_3$ , the sulphur globule oxidised by adding  $KClO_3$  crystals, then heated with  $H_2SO_4$  till fumes come off.

The voltage of the hot solution is 2 to 2.5 volts. A straight platinum wire was first tried as cathode, but metallic lead deposited on it. Also with 1 ampère of current metallic lead deposits on the cathode. Even with a weak current in a cold solution there is danger of metallic lead separating. Results are best obtained with a low voltage and low current density.

In the early experiments, whenever lead sulphate was involved, this was changed to carbonate by digestion with ammonium carbonate, and the lead carbonate was dissolved in dilute nitric acid. These steps were soon found to be unnecessary, the simple solution of the lead sulphate in am. acetate greatly shortening the method.—*Journal of Industrial and Engineering Chemistry*, iii., No. 12.

## THE DETERMINATION OF CHROMIUM AND ITS SEPARATION FROM VANADIUM IN STEELS.

By J. R. CAIN.

WHILE attempting recently to determine chromium in chrome vanadium steels, difficulties with some of the usual methods were encountered. If a steel containing chromium as chromate and vanadium as vanadate is titrated against ferrous solutions, using ferricyanide to indicate the point at which all the vanadium and chromium are reduced, and an excess of titrating solution is present, there is sometimes an indefinite end-point, because as soon as some vanadium is reduced to the vanadyl condition this reacts with the ferricyanide indicator, reducing it to ferrocyanide, which then gives the usual colour with the ferric salts present (Cain, *Journ. Ind. and Eng. Chem.*, 1911, iii., 476; other references will be found here). An experienced operator can oftentimes judge the end-point sufficiently closely for practical work, but the difficulty increases with increasing vanadium, and it is almost always necessary to run blanks of various kinds, increasing to that extent the uncertainties of such methods. If the excess of ferrous solution is titrated back with permanganate some correction is also necessary for chromium oxidised by permanganate (Cain, *loc. cit.*). If in the preliminary oxidation of the vanadium and chromium any manganese dioxide separates, as where potassium permanganate or potassium chlorate are used, some chromium may be, and often is, carried down by the manganese (Arnold and Ibbotson, "Steel Works Analysis," 3rd Ed., p. 180; also Cain, *loc. cit.*). If, in order to separate vanadate from chromate, the nitric acid solution of the steel (with or without preliminary ether extraction of most of the iron) is poured into excess of sodium hydroxide solution and boiled, usually an appreciable amount of chromium goes into the filtrate with the vanadium. Many methods take no account of this chromium. The amount so lost increases with the manganese in the steel and the time of boiling, the manganese being converted in part to peroxide, and this, in the strongly alkaline solution, oxidising the chromium to chromate (Cain, *loc. cit.*).

Many careful tests having shown that chromium in much larger amount than the usual commercial steels carry can be precipitated completely in a few minutes by boiling the nearly neutralised (ferrous) solution of the steel with barium carbonate, cadmium carbonate, zinc oxide, or magnesium oxide, it was decided to base a method for determining chromium on one of these methods of separation from iron. Probably the reason why such separations have not come into more general use is because practically all writers have directed to make the carbonate or oxide precipitation in the cold, which requires many hours' standing, and is even then sometimes incomplete. The work done here has shown that but ten or fifteen minutes' boiling, with proper precautions, is all that is ever necessary, the filtrates being free from even traces of chromium (or vanadium).

Noyes and Bray (*Technology Quarterly*, 1908, xxi., 14) have given conditions for completely precipitating chromates in the presence of vanadates which make possible a good separation of the two elements. The work here having completely confirmed their results, this separation was incorporated in the method.

### Description of the Method.

Dissolve in a covered 300 cc. Erlenmeyer flask an amount of drillings, which will give not to exceed 6 or 7 centigrms. of chromium, using about 10 cc. of concentrated hydrochloric acid per gm. of steel. The concentrated acid (specific gravity 1.20) seems to dissolve the steel much more readily than a diluted acid. When no more hydrogen is given off, dilute to 100 or 150 cc. with hot water, nearly neutralise with saturated sodium carbonate solution, add barium carbonate emulsion in slight



excess, place on the hot plate and boil vigorously ten or fifteen minutes, with small additions of the barium carbonate emulsion every two or three minutes. The flask should be kept covered during all operations so as to exclude air as completely as possible. Too great an excess of barium carbonate should not be used, as this increases the difficulty of extracting the chromium in the subsequent fusion. An excess of a gram or two is the most that should be present. Remove the flask from the plate, let the precipitate settle, and filter at once on a 11 cm. white label, No. 589 filter, washing twice with hot water. These operations should be carried out rapidly and without delay. Place the filter and precipitate in a sufficiently large platinum crucible, burn off the filter, add 2 grms. of sodium carbonate and about one-fourth gram. potassium nitrate, and fuse for twenty minutes. Support the inverted and inclined crucible on a glass triangle which has glass legs about three-quarter inch long fused to its corners for supports, place on the bottom of a 250 cc. beaker, cover it with boiling water, and digest a few minutes until the fusion is disintegrated. Filter into a flask, add 1 or 2 cc. of hydrogen peroxide to the filtrate, and boil for five or ten minutes to destroy the excess of peroxide. Cool, transfer to a 250 or 300 cc. separatory funnel, add a slight excess of nitric acid (1 : 1), and shake vigorously a few minutes, allowing the liberated carbon dioxide to escape by inverting the separatory funnel and opening the stopcock. Transfer to a 250 cc. beaker, just neutralise with sodium hydroxide solution, and then add nitric acid (1 : 1), 2 cc. for each 100 cc. of solution. Add 20 cc. of a 20 per cent lead nitrate solution to the cold solution, stirring vigorously. The precipitate settles quickly. It is filtered on asbestos, and washed three or four times with cold water. The asbestos mat is transferred to a beaker or flask, and the lead chromate decomposed with hot hydrochloric acid (1 : 4). The solution is cooled, the volume made up to 150 or 200 cc., and it is titrated approximately N/10 ferrous sulphate solution with ferricyanide as outside indicator. Or, if desired, an excess of the ferrous sulphate solution is added, and the excess titrated back against bichromate. The standard iron solution should be compared with bichromate or permanganate on the day it is used. Table I. gives results obtained with synthetic solutions and with the chrome-vanadium standard steel of the Bureau of Standards. The synthetic solutions were made by adding the chromium from a carefully standardised bichromate solution, and the vanadium from a sodium vanadate solution to the hydrochloric acid solution of a vanadium and chromium free steel.

TABLE I.

| No. of expt. | Iron present. Grms. | Vanadium present. | Chromium present. | Chromium found | Difference. |
|--------------|---------------------|-------------------|-------------------|----------------|-------------|
| 1.           | I                   | 0.0012            | 0.0140            | 0.0137         | -0.0003     |
| 2.           | I                   | 0.0024            | 0.0280            | 0.0277         | -0.0003     |
| 3.           | I                   | 0.0024            | 0.0420            | 0.0420         | 0.0000      |
| 4.           | I                   | 0.0036            | 0.0560            | 0.0558         | -0.0002     |
| 5.           | I                   | 0.0048            | 0.0700            | 0.0700         | 0.0000      |
| 6.           | I                   | 0.0060            | 0.1120            | 0.1122         | +0.0002     |
| 7.           | I                   | 0.0120            | 0.1680            | 0.1685         | +0.0005     |
| 8.           | I                   | 0.0180            | 0.2800            | 0.2805         | +0.0005     |
| 9. (a)       | 4                   | —                 | —                 | 0.0536         | —           |

(a) Chrome-vanadium standard: 4 determinations; each gave 1.34 per cent. Average of results of co-operating analysts: per cent chromium 1.36; per cent vanadium 0.204

#### Notes and Precautions.

Numbers 6, 7, and 8 of Table I. show that very large amounts of chromium can be completely precipitated by the barium carbonate method carried out as above described.

However, if the amount of chromium exceeds that recommended in the method described herein, it cannot be readily extracted by 2 grms. of sodium carbonate, particularly if too great an excess of barium is present. The amount of sodium carbonate used was governed by the directions of Noyes and Bray (*loc. cit.*, p. 48, Note 4) who state that, for a successful separation of chromium, not too much sodium nitrate should be present. The separations described herein were made in a volume of 250 cc., and inasmuch as 2 grms. of sodium carbonate were used for fusions, the resulting sodium nitrate concentration was about 1.3 gram. per 100 cc. The filtrates were tested for chromium by removing the excess of lead with sulphuric acid, filtering, concentrating to about 10 or 15 cc., and making alkaline with sodium hydroxide. No colour indicative of chromate was ever obtained, even after adding a little hydrogen peroxide and boiling to oxidise any chromium that may have been reduced. Possibly the larger amounts of chromium could have been completely extracted by one fusion had more sodium carbonate been used, but the manipulation is then less convenient; moreover, with the usual range of chromium content in commercial steels one need never work with more than 7 or 8 centigrams. to secure an accurate determination.

The boiling with hydrogen peroxide in alkaline solutions before precipitation with lead nitrate is done in order to destroy any nitrite formed during the fusion. If this were present when the solution is acidified, the resulting nitrous acid would possibly reduce some chromium or vanadium. Five minutes' boiling will insure destruction of the excess of peroxide if only 2 or 3 cc. of the usual 3 per cent solution are used. The hydrogen peroxide should be completely removed before acidifying, inasmuch as it reduces chromic acid. (Perchromic acid is first formed, but is rapidly decomposed).

The freeing of the solution from carbon dioxide is an important step, for if this is not done the precipitate does not settle out rapidly, and is not so easy to filter; shaking in a separatory funnel, as described, is a convenient way of accomplishing this.

The solutions containing the chromium, after titration, were treated with enough sulphuric acid to precipitate the lead, which was filtered off and washed with dilute sulphuric acid. The filtrates were evaporated on the hot plate until free from hydrochloric acid, and then electrolysed with a mercury cathode until free from iron and chromium (Cain, *loc. cit.*). The solution in the electrolysis apparatus was then tested for vanadium by hydrogen peroxide, none being found in most cases, and in others only traces, showing that the separation under the conditions given is practically perfect. It is well to examine the insoluble from the fusion for chromium by again fusing it with sodium carbonate and potassium nitrate. The solution from the second fusion is almost invariably colourless when working under the conditions herein recommended. Should there be a slight yellow colour, however, the chromium causing it can be estimated colorimetrically. A determination of chromium can be made easily in one and a-half hours.

#### Conclusions.

1. Sources of error in some of the usual methods for determining chromium in chrome or chrome-vanadium steels, which limit the accuracy of the results, are described.

2. The precipitation of chromium from solutions of steels, and its separation from practically all the iron, can be effected quickly and easily by boiling with a number of precipitants herein described.

3. The chromium may be readily extracted from the precipitates by fusion, and separated from vanadium by precipitating as lead chromate, under the conditions prescribed.—*Journal of Industrial and Engineering Chemistry*, iv., No. 1.

## PROCEEDINGS OF SOCIETIES.

## ROYAL SOCIETY.

Ordinary Meeting, April 25th, 1912.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

*"Diffusion and Mobility of Ions in a Magnetic Field."* By J. S. TOWNSEND, F.R.S.

The mobility and diffusion of ions in a magnetic field is investigated on the same principles as those employed in the ordinary kinetic theory by considering the motion of an ion along its free paths between collisions with molecules. If  $U$  and  $K$  be the mobility and coefficient of diffusion when the magnetic force is zero,  $U_h$  and  $K_h$  the corresponding quantities in directions at right angles to a magnetic force  $H$ , then  $U_h = \frac{U}{1 + \omega^2 T^2}$  and  $K_h = \frac{K}{1 + \omega^2 T^2}$ , where  $\omega = He/m$  and  $T$  the mean interval between collisions.

The magnetic deflection  $\theta$  of a stream of ions moving with a constant velocity in an electric field is also investigated, and a method is indicated of determining the velocity  $U$  due to an electric force  $X$ . When  $\theta$  is small,  $\tan \theta = HU/X$ , and when  $\theta$  is large,  $\tan \theta X = HU_h$ .

*"Observed Variations in the Temperature Coefficients of a Precision Balance."* By J. J. MANLEY, M.A.

In this paper is given an account of experiments which supplement and extend an earlier research (*Phil. Trans.*, A, ccx., 387) dealing with changes which may be observed in the resting-points of precision balances.

Attention is directed to the following:—

- The possibility of the change from a positive to a negative value for the temperature coefficient of a balance.
- The critical temperature range of a balance.
- The various causes tending to give rise to a temperature coefficient.
- The necessity for the "ageing" of a beam either naturally or artificially.

In addition to the above, certain minute and temporary lateral displacements of the whole beam are investigated. A method for measuring these movements is given, and their origin disclosed.

*"Torque produced by a Beam of Light in Oblique Refraction through a Glass Plate."* By Dr. GUY BARLOW, D.Sc.

In accordance with the principle that light carries with it a stream of momentum, the passage of a beam of light through a refracting plate should give rise to a torque on the plate, it being supposed that the reaction is on the matter through which the beam is passing. In 1905, Prof. Poynting and the author made experiments which confirmed this result, but as disturbances, due to gas action, were not eliminated, more exact measurements appeared desirable. In the present experiment the original double prism arrangement was abandoned in favour of a single cube. A glass cube, of 1 cm. edge, was suspended axially by a fine quartz fibre. A strong beam of light was sent obliquely through the cube, the angle of incidence having been so adjusted that the beam entered through one half of one face, and emerged through the half face diagonally opposite. The torque was determined from the observed angular deflection of the cube. Observations were made in hydrogen and air with pressures ranging from 0.1 to 76 cm. Hg. The disturbance due to radiometer action was found to be inversely proportional to the gas pressure, and could be eliminated. After allowing for the reflected beams, the observed torque (of the order  $2 \times 10^{-6}$  dyne cm.) was within 2 per cent of that calculated from the energy of the beam.

*"Contributions to the Study of Flicker."* Paper III. By T. C. PORTER, M.A., D.Sc.This paper is a continuation of two former papers: *Proc. Roy. Soc.*, lxiii., 347, and lxx. 313.

If  $n$  be the number of revolutions per second for a disc with white sector " $w$ " and the rest black, just to appear flickerless under illumination " $I$ ," then  $n = -27.83 + (8.57 + 2.79 \log I) \log w(360 - w)$ ; this holds when  $I$  is greater than 3.98. If  $I$  be less than 3.98, then  $n = -38.6 + (12.4 + 0.77 \log I) \log w(360 - w)$ .

The existence of the remarkable break in the line connecting  $n$  and  $\log I$  for  $w = 180$  has been confirmed.

The influence of the variation of the pupil of the eye with the illumination is discussed, and a photograph of eyes, as in complete darkness, is given.

The relation of  $n$  and  $I$  for perfectly symmetrical discs of four or more sectors is established, and application made to the measurement of high illuminations.

Asymmetrical discs are next considered, and it is proved that  $n$  is independent of the direction of their rotation.

It is next shown that a flickerless disc of white sector " $w$ " under illumination  $I$  appears as bright as an all-white disc under illumination  $\frac{I \times w}{360}$ .

If " $m$ " be the magnitude of the maximum black sector which can be inserted into an otherwise white disc without affecting its albedo when rotating flickerless under illumination  $I$ , it is proved that  $m = 12.2 - 6.8 \log I$ , and this is applied to show how accurate readings may be obtained with common forms of photometer, in spite of a "blind region" in which the eye is unable to judge differences of apparent brightness.

The variations in retinal excitation during the slowly increasing speed of rotation of a part white, part black, disc are next described, and it is shown how the value of  $m$  influences that of  $n$  for which flicker just vanishes.

A method is given for finding  $m$  for various discs, with an experimental verification.

Lastly, with the aid of a reasonable assumption, there is deduced a curve expressing numerically the rise and fall of retinal excitation with time when the eye has presented to it suddenly a white surface, which is afterwards suddenly withdrawn. This curve is drawn to scale for a given illumination of the white surface.

## ROYAL INSTITUTION.

Annual Meeting, May 1st, 1912.

Sir JAMES CRICHTON-BROWNE, Treasurer and Vice-President, in the Chair.

THE Annual Report of the Committee of Visitors for the year 1911, testifying to the continued prosperity and efficient management of the Institution, was read and adopted, and the report on the Davy-Faraday Research Laboratory of the Royal Institution, which accompanied it, was also read. Forty-six new members were elected in 1911. Sixty-three Lectures and nineteen Evening Discourses were delivered in 1911. The books and pamphlets presented amounted to about 281 volumes, making with 677 volumes (including periodicals bound) purchased by the Managers, a total of 958 volumes added to the Library in the year.

Thanks were voted to the President, Treasurer, and the Honorary Secretary, to the Committees of Managers and Visitors, and to the Professors, for their valuable services to the Institution during the past year.

The following gentlemen were unanimously elected as Officers for the ensuing year:—

*President*—The Duke of Northumberland.*Treasurer*—Sir James Crichton-Browne.*Secretary*—Sir William Crookes.

*Managers*—Dr. Henry E. Armstrong; The Right Hon. Lord Avebury; J. H. Balfour Browne; W. A. Burdett-



Coutts; Sir David Gill; The Right Hon. The Earl of Halsbury; Dr. Donald W. C. Hood; Alexander C. Ionides; Sir Francis Laking, Bart.; Henry F. Makins; The Right Hon. Viscount Iveagh; Sir Alexander C. Mackenzie; Alan A. Campbell Swinton; Alexander Siemens; and The Right Hon. Sir James Stirling.

*Visitors*—Dugald Clerk; Francis Darwin; William A. T. Hallows; Dr. A. Croft Hill; W. Adams Frost; H. R. Kempe; Joseph G. Gordon; Charles Edward Groves; Robert Kaye Gray; Sir Robert Hadfield; Carl E. Melchers; Major Percy A. MacMahon; William Stone; Major G. J. W. Noble; and Harold Swithinbank.

# CHEMICAL SOCIETY.

Ordinary Meeting, April 18th, 1912.

Prof. PERCY F. FRANKLAND, LL.D., F.R.S., President,  
in the Chair.

THE PRESIDENT referred to the loss the Society had sustained by the deaths of Dr. Edward Divers, F.R.S., and Mr. John Pattinson, who had served on the Council and as Vice Presidents of the Society.

It was announced that the following Committees for 1912-1913 have been appointed by the Council:—

*Finance Committee*—Messrs. E. G. Hooper, G. T. Moody, Sir Edward Thorpe, Sir William Tilden, and the Officers.

*House Committee*—Messrs. W. R. Dunstan, R. Messel, J. E. Reynolds, J. M. Thomson, Sir Edward Thorpe, Sir William Tilden, and the Officers.

*Library Committee*—Messrs. B. Dyer, W. Gowland, A. Harden, J. T. Hewitt, C. A. Keane, A. R. Ling, R. Meldola, E. J. Mills, J. C. Philip, J. M. Thomson (Chairman), Sir William A. Tilden, J. A. Voelcker, the Editor, and the Officers.

*Publication Committee*—Messrs. H. B. Baker, J. N. Collie, F. G. Donnan, B. Dyer, M. O. Forster, C. E. Groves, A. McKenzie, J. C. Philip, and the Officers.

*Research Fund Committee*—Messrs. H. B. Baker, W. R. Bousfield, J. N. Collie, H. B. Dixon, J. J. Dobbie, M. O. Forster, A. Liversidge, R. Meldola, W. J. Pope, J. E. Reynolds, and the Officers.

Certificates were read for the first time in favour of Messrs. Thomas Alcock, The Rookery, Pye-Bridge, Alfreton; Raymond Theodore Fred Barnett, B.Sc., 19, Merton Street, Swindon; Charles James Vinall Bews, B.Sc., 52, Sir John's Road, Selly Park, Birmingham; Harry Brindle, 225A, Oxford Road, Manchester; Frank Lothian Cheshire, Mines Department, Brisbane, Queensland; Alfred George Ernest Foster, 103, St. Mark's Road, Bristol; Madanlal Jekisandas Gajjar, M.A., Heira House, Girgaum, Bombay; Michael Francis Gallogly, B.A., St. Colman's College, Newry; Robert Glegg, B.Sc., 19, Mount Street, Aberdeen; Edmund Haworth Holden, M.Sc., 25, Curwen Street, Workington; Edwin Oliver James, The Curatage, Low Moor; Harold E. Kuntzen, Doric Lodge, Clapton Common, N.; James Leslie Auld Macdonald, B.Sc., 13, Howard Place, St. Andrews; Nadirshaw Adarji Masani, M.A., B.Sc., Baroda Camp, India; Harold McKee Langton, B.Sc., 80, Kingston Road, Ilford; George Mason Williams, 17, Springcroft Avenue, Muswell Hill, N.

Certificates have been authorised by the Council for presentation to ballot under By-law I. (3) in favour of Messrs. Jatindranath Chakraborty, Goabagan, Calcutta; Frederick George Whittick, Imperial Provincial College, Chinanfu, Shantung.

Of the following papers, those marked \* were read:—

\*70. "Studies on Platinocyanides." By LEONARD ANGELO LEVY.

The action of bromine on potassium platinocyanide has been re-investigated, and it is found that Hadow's

explanation of the reaction is correct, but that the constitution of the resulting product is represented by  $6K_2Pt(CN)_4 \cdot K_2Pt(CN)_4 \cdot Br_2$ , instead of the 5:1 formula given by him.

Lead and manganese dioxides oxidise potassium platinocyanide in the presence of dilute sulphuric acid yielding a compound similar to the bromine additive product, in which  $Br_2$  is replaced by  $SO_4$ . The salt behaves like the sulphate of a feebly electro-positive element, and undergoes double decomposition with barium salts.

Hydrogen peroxide (and other peroxides in which the oxygen atoms are supposed to be linked in a chain) oxidises platinocyanides in the presence of dilute sulphuric acid, with the removal of one atom of the basic metal, forming compounds of the type  $MPt(CN)_4$ . These immediately combine with unchanged platinocyanide with the production of well defined crystallised double salts. The potassium compound has the composition  $3K_2Pt(CN)_4 \cdot KPt(CN)_4 \cdot 6H_2O$ . These double salts are not acted on by hydrogen peroxide, hence the product of the reaction is a platino-platinocyanide of this type. An exception is afforded by hydroplatinocyanic acid, in which the combination is so feeble that the action of hydrogen peroxide completely oxidises this substance to the compound  $HPt(CN)_4$ .

The combination between the platino- and platinocyanide is destroyed by oxidation with "perhydrol," the platinocyanide being completely oxidised to the form  $MPt(CN)_4$ . These salts are true platinocyanides, bearing a relationship to platinocyanides similar to that existing between ferro- and ferri-cyanides. They may be regarded as compounds of the cyanides with platinum tricyanide,  $MCN \cdot Pt(CN)_3$ . The oxidation of hydroplatinocyanic acid by hydrogen peroxide (6 per cent) or "perhydrol" affords the readiest method of preparing the platinocyanides. Direct oxidation of metallic platinocyanides yields products which are mixed with the sulphate of the basic metal, and this is often very difficult to separate.

## DISCUSSION.

Prof. EMERSON REYNOLDS congratulated Mr. Levy on his efforts to clear up the nature of some of the oxidation products of platinocyanides, although much still remained to be done. As illustrating this, he mentioned a curious observation of Sir J. Dewar's, that an old specimen of supposed platinocyanide of lithium became red when cooled in liquid air, and lost the red colour when restored to the ordinary temperature. At Sir J. Dewar's request the speaker examined the specimen, which was nearly colourless—unlike pure red freshly prepared hydrated platinocyanide of lithium, which is bright green, and does not become red in liquid air. It had evidently undergone more or less oxidation in presence of a considerable excess of lithium cyanide, &c. This material when cooled in liquid air was seen to owe its red tint to minute red crystals distributed throughout, which were colourless at the ordinary temperature. The crystals closely resembled a large orange-red crystal which the speaker had in his collection, and believed to be an oxidation product of a platinocyanide, having the formula  $Li_2Pt(CN)_5 \cdot 2H_2O$ . This salt gave a colourless solution in water, from which colourless crystals were obtained, exhibiting a delicate lavender fluorescence; these contained 3 molecules of water of crystallisation. When cooled in liquid air these behaved just like Sir J. Dewar's salt, and gave the red dihydrate. On prolonged cooling a yellow monohydrate was formed as the red colour faded out. This remarkable example of successive dehydration by exposure to very low temperatures was reversed in presence of moisture as the normal temperature was reached. No compound exhibiting these characteristic properties had yet been met with among Mr. Levy's products, but the author would doubtless turn his attention in that direction, and the speaker hoped that he would obtain some clue to the constitution of the compound to which he (Prof. Reynolds) had now drawn their attention.





been studied on the same lines as the parent substance (see *Trans.*, 1910, xcvi., 1438, 2025; 1911, xcix., 792, 1306, 1486).

78. "Aromatic Antimony Compounds. Part IV. Compounds of Antimony Trichloride with Diazonium Chlorides." By PERCY MAY.

Several additive compounds of antimony trichloride with various diazonium chlorides have been prepared. These compounds, which crystallise well, are insoluble in water, and more stable than the parent diazonium chlorides. The decomposition products of these substances were also described.

79. "Note on the Constituents of Rhubarb." By FRANK TUTIN and HUBERT WILLIAM BENTLEY CLEWER.

In a former communication (*Trans.*, 1911, xcix., 962) the authors described the isolation from rhubarb of a small amount of a substance (m. p. above 340°), which yielded an acetyl derivative melting at 335°.

It has since been ascertained that this substance is identical with the phenolic compound, jambulol, which has quite recently been described by Power and Callan (*Pharm. Journ.*, 1912, [4], xxxiv., 416).

Jambulol possesses the empirical formula  $C_{16}H_{13}O_4(OH)_5$ , but its molecular weight could not be determined owing to its sparing solubility.

80. "Molecular-weight Determinations from the Relative Lowering of the Vapour Pressure of Ethereal Solutions." By ROBERT WRIGHT. (Will be inserted in next issue).

81. "Electrolytic Reduction. Part I. Unsaturated Aldehydes and Ketones." By HERBERT DRAKE LAW.

A large number of unsaturated aldehydes and ketones have been reduced on lead cathodes by the electrolytic method. The reaction takes place in stages, and commences at either the double linking or the carbonyl radicle. The products are saturated alcohols, unsaturated alcohols, or ketones of approximately the same molecular weight of the original substance, together with diketones and pinacones of double the molecular formula. The reaction proceeds quite readily with aliphatic and alicyclic compounds in either acid, alkaline, or neutral solvents. Reduction is most rapid when acid electrolytes are used, but products combined with the lead of the cathode are formed. The latter phenomenon is quite general with the compounds examined in both aliphatic and alicyclic series, and greatly interferes with the usefulness of the reaction. The substances easiest to reduce are those containing the double linking and the carbonyl groups in adjacent positions. The separation of these two groups greatly reduces the reactivity, and compounds with only one of the groups are moderately stable. The two double linkings therefore mutually exalt the properties of the other when brought close together, but still retain their individuality.

82. "A Method of Estimating Potassium Iodate." By JAMES ECKERSLEY MYERS.

When solutions of potassium iodate and oxalic acid are mixed together, or the substances suspended in water, a slight yellow colour is developed after several hours at the ordinary temperature.

On heating the mixture to 80°, a vigorous reaction commences, and continues without any further application of heat, with the evolution of carbon dioxide and iodine.

This reaction was examined quantitatively by Chrétien (*Ann. Chim. Phys.*, 1898, [7], xv., 358), and he found that the whole of the iodine present in the iodate was evolved in the free state, but gave no figures to indicate the degree of accuracy of the method. The present method is similar to Chrétien's, but can be carried out much more quickly. (The work described in the present communication was carried out in ignorance of Chrétien's investigation).

A weighed amount of pure potassium iodate is placed together with an excess of pure oxalic acid in a flask fitted with a ground-glass joint, which carries the exit tube. A tube for conducting steam into the flask is sealed into the side of the neck, and reaches nearly to the bottom of the

flask. The arrangement of these tubes prevents the existence of the cul-de-sac which exists in an ordinary steam-distillation apparatus, and so allows the iodine to be swept out by the steam without obstruction. Steam is passed into the mixture so as to attain the temperature of reaction. When the iodine commences to be evolved, the flow of steam is slackened, and the iodine gradually swept out of the flask into a receiver cooled in ice, containing potassium iodide solution. If desired, this solution may be replaced by a mixture of potassium iodide and a known volume of standard sodium thiosulphate. After a short time the contents of the reaction flask become quite colourless, and no iodine remains in the delivery tube. After the steam has been stopped, the receiver is removed, and the tip of the delivery tube washed, the washings being placed in the receiver. If the iodine is collected in potassium iodide, this is titrated with standard sodium thiosulphate solution; if collected in thiosulphate solution the excess of this reagent is titrated with standard iodine. In either case a measure of the amount of iodine produced in the reaction is obtained. The following table shows the amounts of iodate used (a), the amounts of iodine produced (b), together with the ratio (a/b) :—

TABLE I.

|    | a (grm.). | b (grm.) | a/b.  |
|----|-----------|----------|-------|
| 1. | 0.283     | 0.168    | 1.684 |
| 2. | 0.306     | 0.182    | 1.681 |
| 3. | 0.486     | 0.292    | 1.674 |
| 4. | 0.500     | 0.296    | 1.689 |
| 5. | 0.601     | 0.357    | 1.683 |
| 6. | 0.659     | 0.389    | 1.690 |
| 7. | 0.994     | 0.589    | 1.687 |

The value for the ratio will be seen to be practically constant, and it agrees very well with the ratio  $2KIO_3/12$ , the calculated value of which is 1.685.

The next table shows a comparison of the amounts of iodine calculated on the assumption that two molecules of potassium iodate produce one molecule of iodine (a), with the amounts of iodine experimentally determined (b). A is the weight of iodate used.

|    | A (grm.) | a (grm.). | b (grm.). |
|----|----------|-----------|-----------|
| 1. | 0.283    | 0.168     | 0.168     |
| 2. | 0.306    | 0.181     | 0.182     |
| 3. | 0.486    | 0.288     | 0.292     |
| 4. | 0.500    | 0.296     | 0.296     |
| 5. | 0.601    | 0.356     | 0.357     |
| 6. | 0.659    | 0.391     | 0.389     |
| 7. | 0.994    | 0.589     | 0.589     |

The effects of various salts on the reaction are as follows :—

**Potassium Nitrate.**—The amount of iodine produced as determined by titration is too high, probably owing to the formation of a little nitric acid which passes over to the potassium iodide solution and liberates iodine.

**Potassium Chromate and Sulphate.**—These salts do not affect the reaction.

**Potassium Chloride and Chlorate.**—These salts prevent the formation of iodine, although in the case of chlorate carbon dioxide is given off.

**Potassium Bromate.**—On gently warming the mixture to about 30°, the bromate and oxalic acid react to form bromine and carbon dioxide. After some time the bromine ceases to be evolved, and the solution may be almost freed from bromine by gentle warming. On heating to about 80° the iodate and oxalic acid react to produce iodine and carbon dioxide. This reaction presents a convenient method of detecting, quantitatively, a mixture of potassium bromate and iodate.

The action of oxalic acid on potassium bromate, both alone and in presence of other salts, is under investigation.

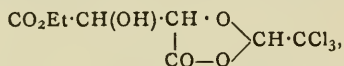
83. "The Action of Sodium Hyposulphite on Copper Sulphate in Aqueous Solution." By JAMES BRIERLEY FIRTH and JAMES ECKERSLEY MYERS.

This reaction has been examined under various conditions, and it has been found that the final products vary with the relative amounts of the reacting substances. When the copper salt is in excess the product is chiefly metallic copper, and this may be precipitated in a very active form, which on exposure to the air becomes light brown, and has then a composition indicating the presence of cuprous oxide. If the sodium hyposulphite is in excess, the product is chiefly cupric sulphide. The authors are unable to confirm the observation of Schützenberger that copper hydride is produced in the reaction.

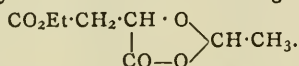
An improved form of the apparatus used for precipitating, filtering, and drying in an inert gas was used in this investigation.

84. "The Action of Chloral on Ethyl Tartrate and on Ethyl Malate." By THOMAS STEWART PATTERSON and ANDREW McMILLAN.

Chloral condenses with ethyl tartrate to give an additive compound of the formula—



and with ethyl malate to furnish the analogous compound,

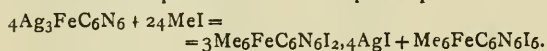


85. "The Alkylation of the Ferro- and Ferric-cyanides." By ERNOLD GEORGE JUSTINIAN HARTLEY.

Methyl sulphate reacts with potassium ferricyanide at 100°, reduction taking place, and the same products are obtained as when the ferrocyanide is employed.

Methyl iodide when heated with silver ferrocyanide in a sealed tube forms a compound,  $\text{Me}_6\text{FeC}_6\text{N}_6\text{I}_2 \cdot 4\text{AgI}$ , which is decomposed by nitric acid or silver nitrate into the compound,  $\text{Me}_6\text{FeC}_6\text{N}_6(\text{NO}_3)_2$ , and silver iodide. When silver ferricyanide and methyl iodide are similarly treated, reduction takes place according to the equation  $\text{Ag}_3\text{FeC}_6\text{N}_6 + 6\text{MeI} = \text{Me}_6\text{FeC}_6\text{N}_6\text{I}_2 + 3\text{AgI} + \text{I}_2$ .

The hexamethylferrocyanogen iodide then combines partly with the silver iodide and partly with the free iodine to form a periodide. The complete equation is—



86. "Nitrites of the Alicyclic Ammonium Series. Part I. Nitrosopiperazinium Nitrite." By PRAFULLA CHANDRA RAY and JITENDRA NATH RAKSHIT.

When the filtrate from the double decomposition between piperazinium hydrochloride and silver nitrate in aqueous solution is allowed to evaporate slowly in a vacuum over sulphuric acid, the first crop or two of crystals consists of pure 1:4-dinitrosopiperazine. The last crops are those of nitrosopiperazinium nitrite,  $\text{NO} \cdot \text{N} \begin{array}{c} \diagup \text{CH}_2 \cdot \text{CH}_2 \\ \diagdown \text{CH}_2 \cdot \text{CH}_2 \end{array} \text{NH}_2 \cdot \text{HNO}_2$ .

87. "The Molecular Conductivities of Potassium Nitrite, Mercuric Nitrite, and Potassium Mercurinitrite." By PRAFULLA CHANDRA RAY and NILRATIN DHAR.

From the conductivity measurements of the above salts it would appear that potassium mercurinitrite is almost completely decomposed in aqueous solution into its components, and that it does not consist of kalion, ( $\text{K}^\circ$ ), and mercurinitrosion,  $\text{Hg}(\text{NO}_2)_4$ , as is supposed by Ostwald.

88. "A Method of Estimating Tin in its Ores, Alloys, and Compounds." By MANINDRA NATH BANERJEE and SATISH CHANDRA BANERJEE.

Stannous chloride, prepared from tin ores, alloys, and compounds, is easily titrated with N/10-mercuric chloride solution, the indicator used being potassium iodide solution. The solution is "spotted" on a porcelain tile,

and the end reaction is indicated when a drop of the tin solution under titration colours the iodide yellow owing to excess of mercuric chloride.

90. "The Rate of Reduction of Carbon Dioxide by Carbon." By THOMAS FRED ERIC RHEAD and RICHARD VERNON WHEELER.

The velocity of the reaction  $\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$  at different temperatures has been determined. The velocity of reaction increases with increase of temperature, the mean velocity ratios for a temperature interval of 10° diminishing fairly regularly as the temperature scale is ascended.

Thus, in a series of experiments in which a mixture containing 20 per cent of carbon dioxide and 80 per cent of nitrogen was employed, the following mean values of  $k$  at different temperatures were obtained ( $k = \frac{1}{t} \cdot \log \frac{\text{C}_0}{\text{C}_t}$ ):

| Temperature. | $k(t-1 \text{ minute})$ . |
|--------------|---------------------------|
| 900°         | 0.00060                   |
| 950          | 0.00374                   |
| 1000         | 0.01764                   |
| 1050         | 0.05760                   |
| 1100         | 0.10570                   |

The mean velocity ratios for an interval of 10°, obtained from the expression  $\frac{k_{t+10}}{k_t} = 10^{10b}$ , are given in the following table, together with the values of  $b$  obtained from the experimental numbers.

| Temperature range. | $b$ .   | $k_{t+10}/k_t$ . |
|--------------------|---------|------------------|
| 900—950°           | 0.01589 | 1.44             |
| 950—1000           | 0.01346 | 1.36             |
| 1000—1050          | 0.01028 | 1.27             |
| 1050—1100          | 0.00527 | 1.13             |

(To be continued)

## SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, May 1st, 1912.

Mr. LEONARD ARCHBUTT, President, in the Chair.

MESSRS. Reginald Freeman Easton and Leonard Goodban were elected members of the Society.

Certificates were read for the first time in favour of Messrs. Stanley Winter Collins, 42, Landford Road, Putney, S.W., and Charles Blüthner Lessner, Carril, Spain.

Certificates were read for the second time in favour of Messrs. Harold Thomas Cranfield, Ernest Gabriel Jones, and William Henry Roberts.

The following papers were read and discussed:—

"Analysis of Lithopone." By W. L. AUSTIN and CHARLES A. KEANE.

The method of analysis recommended consists in treating the sample with hydrochloric acid, filtering off the barium sulphate, and estimating the total zinc volumetrically by titrating with potassium ferrocyanide in presence of tartaric acid and ammonia; a reliable determination can thus be made in presence of iron. For the estimation of the zinc present as sulphide a separate portion of the sample is oxidised with bromine, and the resulting zinc sulphate precipitated with barium chloride after previously removing the original barium sulphate by filtration. The result is calculated to zinc sulphide, and the zinc present as oxide calculated by difference from the two estimations. The total barium sulphate, zinc sulphide, and zinc oxide are thus determined. The method is rapid, sufficiently accurate for the technical analysis of lithopone, and avoids the lengthy estimation of the zinc as sulphide.



"Effect of Lime on the Ammonium Molybdate Method of Lead Assay." By C. O. BANNISTER and W. McNAMARA.

Considerable differences of opinion are found to exist in published work on the effect of lime on Alexander's method of lead assay.

The authors have determined the effect of the addition of progressive amounts of a solution of calcium sulphate in ammonium acetate to a solution of lead sulphate to be titrated, and have found increasingly high results up to a certain limiting point, after which further additions of the calcium solution make no difference. The highest reading thus obtainable being 114.4 per cent of the lead actually present, which corresponds to the precipitation of the compound  $7\text{PbMoO}_4\text{CaMoO}_4$ .

"Constituents of Oil of Savin." By J. WATSON AGNEW and ROBIN B. CROAD.

The oil contains sabinene, terpinene, sabinol acetate and formate, and a small quantity of the ester of another acid. Several samples were found to contain a large quantity of pinene, and one sample contained laevorotatory sabinene and sabinol. The highest yield of sabinene obtained was 16 per cent.

"Detection of Heavy Petroleum in Paints and Vegetable Oils." By W. B. POLLARD.

The author describes a modification of the ordinary saponification process for the detection of heavy petroleum in paints and vegetable oils. Saponification is effected by adding the paint or oil to be examined to molten caustic soda, and then extracting the fused mass with light petroleum. It is claimed that as little as 1 per cent of heavy petroleum can be detected in linseed-oil by this method.

## CORRESPONDENCE.

### DISINFECTANT CONTRACTS.

To the Editor of the Chemical News.

SIR,—One of your contemporaries recently published an article entitled "Contract Conditions as to Disinfectants," in which stress was very properly laid on the importance of ascertaining the efficiency of disinfectants. It is obvious enough that local authorities and others who purchase disinfectants without checking their germicidal properties are only encouraging those manufacturers of so-called disinfectants which do not and cannot disinfect, who flourish at the expense of ignorant buyers.

But while I fully agree as to the necessity of inserting guarantee clauses in contracts for the supply of disinfectants, I am bound to point out that none of the specimen clauses quoted in the article referred to would satisfy many of our leading chemists. Those clauses insist only (1) on a guaranteed carbolic acid coefficient ascertained by the Rideal-Walker method; and (2) on proof that the disinfectant when mixed with water will not separate out on standing. Both these tests are fair and proper, but they are not enough. The real value of a disinfectant can only be ascertained when it is tested with water containing salt to represent the hard, brackish, and bad waters met with in the usual working circumstances under which disinfectants are diluted. In short, it is a farce to judge the value of a disinfectant in distilled water and under conditions which only obtain in the laboratory.

Your contemporary was daring enough to write that any disinfectant with a satisfactory Rideal-Walker coefficient must necessarily be sufficient for all germicidal purposes. Such a statement by itself is manifestly absurd, and enlightened buyers know perfectly well that other considerations must be taken into account. As I write I have before me two typical tender forms. The first, issued by an important English borough, stipulates that the disinfectant fluid must be "mixable with water and saline solution in all proportions." The second, from one of the

leading Indian railway companies requires that the fluid "must form a perfect emulsion when mixed with water, whether impure, hard, soft, sea-water, or ordinary water mixed with 5 ozs. of common salt per gallon." No reputable manufacturer can take objection to these requirements, which are absolutely essential if the value of a disinfectant is to be ascertained under ordinary working conditions.—I am, &c.,

CHEMIST.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. cliv., No. 12, March 18, 1912.

Phenyl, *p*-Tolyl, and Diphenyl-oxyhomocampholic Acids, and their Transformation into Benzylidene, *p*-Tolylidene, and Diphenylmethane Camphors.—A. Haller.—Like benzylidene camphor, its higher homologue *p*-tolylidene camphor and diphenylmethyle camphor can be hydrated by halogen acids, giving rise to  $\alpha$ -oxyacids, the specific rotatory power of which is decidedly lower than that of the original substances. With acetyl chloride the acids thus obtained are again dehydrated, yielding the original substances. The increase of the rotatory power which these acids undergo when they are dehydrated approaches that which the author and M. Desfontaines have observed in the case of the ethers of the  $\beta$ -methyl-adipic acids, when cyclic ethers are formed from them.

Decomposition of Uric Acid by Radium Emanation.—P. Mesernitsky.—Radium emanation decomposes sodium mono-urate, ammonia being the final product. The nature of the intermediate products is uncertain. The  $\alpha$ -rays produce the decomposition, while the penetrating rays have no effect; oxygen plays no part in the decomposition.

Determination of Phosphoric Acid in presence of Colloidal Silicic Acid.—P. Mëlikoff and M. Becaia.—The authors have already described a method of separating phosphomolybdates from silicomolybdates by means of a mixture of equal volumes of hydrogen peroxide and ammonium nitromolybdate (*Comptes Rendus*, cliii., 1478). They now find that the same permolybdic reagent can be used to determine phosphoric acid in presence of colloidal silicic acid, and gives very accurate results.

Ethylene Isomerism of Acetylene Dichloride.—G. Chavanne.—The fixation of chlorine by acetylene gives rise to two isomeric dichlorides, as was to be expected from theoretical considerations. Both of them are capable of fixing two atoms of bromine, the action taking place violently and instantaneously in sunlight, but the two bromides obtained are identical, whereas one should be inactive and the other racemic. Apparently, isomerisation occurs at the moment of the fixation of the bromine by one of the dichlorides of acetylene.

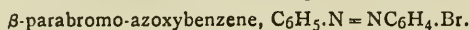
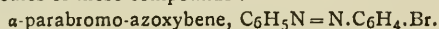
Catalytic Dehydration of Acids of Formic Acid Series by Sulphuric Acid.—J. B. Senderens.—Catalytic dehydration by  $\text{H}_2\text{SO}_4$  occurs with tertiary alcohols with the first term of the series, while it does not begin below the alcohol containing  $\text{C}_5$  of the secondary series and with a still higher homologue among the primary alcohols. These differences are due to the fact that the catalytic activity does not manifest itself below a certain temperature. The limiting temperature is below  $83^\circ$  for tertiary alcohols and about  $118^\circ$  for secondary alcohols. If the alcohols boil at too low a temperature sulphuric acid has no catalytic action on them.

Endoazoic Compounds.—H. Duval.—The author has obtained good yields of *o,o*-bisendoazo-*p,p*-dichlorodi-

phenylmethane by diazotising a sulphuric solution of *o.o*-amino-*p.p*-dichlorodiphenylmethane. The two nitro-derivatives of *o*-aminodiphenylmethane readily give the corresponding monoazo compounds.

*Atti della Reale Accademia dei Lincei.*  
Vol. xxi., No. 3, 1912.

**Azoxycompounds.**—A. Angeli and Bruno Valori.—When azoxybenzene is treated with bromine a monohalogen derivative is obtained. It is readily reduced, losing an atom of oxygen and yielding para-bromo-azobenzene,  $\text{Br.C}_6\text{H}_4.\text{N}=\text{N.C}_6\text{H}_5$ . Thus the original substance is para-bromo-azoxybenzene. When hydrogen peroxide acts on para-bromo-azobenzene it takes up an atom of oxygen, giving a mixture of  $\alpha$ -para-bromo-azoxybenzene, which fuses at  $73^\circ$ , and the  $\beta$ -compound, which fuses at  $92^\circ$ . These two isomers can easily be separated owing to the difference in their solubility in petroleum ether.  $\beta$ -bromo-azobenzene gives para-bibromo-azobenzene when treated with bromine. Similarly *p*-nitro-azobenzene gives *p*-nitro- $\beta$ -bromo-azobenzene. The following structural formulæ probably represent the molecules of these compounds:—



**Thermic Analysis of Binary Mixtures of Chlorides of Divalent Elements.**—Carlo Sandonnini.—Barium chloride gives with manganese chloride a compound containing between 30 and 40 molecules per cent of manganese chloride. Lead chloride gives a single eutectic with cadmium chloride, and also lead bromide with mercury bromide. Cadmium iodide gives mixed crystals in all proportions with mercury iodide.

**Action of Thio-acetic Acid on Cyanguanidine.**—A. Ostrogovich.—When thio-acetic acid acts on cyanguanidine acetyl-thioureido-guanidine is obtained, and from it by the elimination of one molecule of water, methyl-imino-thio-triazine results.

**Supposed Complexity of Tellurium.**—Giovanni Pellini.—Browning and Flint have stated that by a process of fractionation they have separated tellurium into two parts, one of which has an atomic weight below 127.5 and the other above. In a second publication Flint announces that he has obtained a fraction of atomic weight 124.3. The author has repeated the experiments, but with a negative result. The method of electrolytic fractionation also gives a negative result, and in the author's opinion tellurium is an element.

## MISCELLANEOUS.

**Royal Institution.**—On Tuesday next, May 14th, at 3 o'clock, Prof. W. Bateson begins a course of two lectures at the Royal Institution on "The Study of Genetics"; and on Thursday, May 16th, Prof. H. T. Barnes delivers the first of two lectures on "The Physical and Economic Aspects of Ice Formation in Canada." The Friday Evening Discourse on May 17th will be delivered by Mr. W. Duddell, on "High Frequency Currents"; and on May 24th, by Mr. A. D. Hall, on "Recent Advances in Agricultural Science—The Fertility of the Soil."

**Royal Institution.**—A General Monthly Meeting of the Members of the Royal Institution was held on the 6th inst., the Duke of Northumberland, K.G., President, in the Chair. Mr. V. Blagden and Mr. W. A. Harris were elected Members. It was announced that His Grace the President had nominated the following gentlemen as Vice-Presidents for the ensuing year:—The Right Hon. Lord

Avebury; the Right Hon. the Earl of Halsbury; Dr. Donald W. C. Hood; Sir Francis Laking, Bart.; Mr. Henry F. Makins; Mr. Alexander Siemens; Sir James Crichton-Browne (Treasurer); and Sir William Crookes (Honorary Secretary).

**Association of Teachers in Technical Institutions.**—The Annual Conference of the Association of Teachers in Technical Institutions will be held at Whitsuntide in London, at the Polytechnic, Regent Street. A paper will be read by Sir Alfred Keogh, K.C.B., on "The Relations between the Imperial College of Science and Technology and Technical Institutions." There will be a discussion on the important question of the co-operation of employers in Technical Education; a paper on this subject will be read by Mr. E. A. Atkins.

**Ozonair.**—Mr. V. Zingler, for seven years Manager of the Publicity Department of Messrs. Siemens Brothers and Co., Ltd., has been appointed Manager of Messrs. Ozonair, Ltd., 96, Victoria Street, Westminster London, S.W., in succession to Mr. R. Borlase Matthews, Wh.Ex., M.I.E.E., who is joining the General Electric Co., Ltd., 67, Queen Victoria Street, E.C., in order to devote his attention to the promotion of the sale of electric heating and cooking apparatus.

## MEETINGS FOR THE WEEK.

MONDAY, 13th.—Royal Society of Arts, 8. (Howard Lecture). "Heavy Oil Engines," by Capt. H. R. Sankey, R.E.

TUESDAY, 14th.—Royal Institution, 3. "The Study of Genetics," by Prof. W. Bateson, F.R.S.

WEDNESDAY, 15th.—Royal Society of Arts, 8. "Manufacture of Nitrates from the Atmosphere," by E. Kilburn Scott, Assoc.M.Inst.C.E.

Microscopical, 8. "British Enchytraeids—the Genus *Henlea*," by Rev. Hilderic Triand. Exhibition of Pond Life.

THURSDAY, 16th.—Royal Institution, 3. "Ice Formation in Canada," by Prof. Howard T. Barnes, F.R.S.

Royal Society of Arts, 4.30. "Indian Railways," by Neville Priestley.

— Royal Society. "General Theory of Colloidal Solutions," "Tension of Composite Fluid Surfaces and the Mechanical Stability of Films of Fluid," and "Formation of a Heat-reversible Gel," by W. B. Hardy. "Studies on Enzyme Action—XVI., The Enzymes of Emulsin (II.)—Prunase, the correlate of Prunasin; XVII., Enzymes of the Emulsin Type (II.)—The Distribution of  $\beta$ -Enzymes in Plants," by H. E. Armstrong, E. F. Armstrong, and E. Horton. "Studies on Enzyme Action—XVIII., Enzymes of the Emulsin Type (III.)—Linase and other Enzymes in Linacea," by H. E. Armstrong and J. V. Eyre. "Reflex Rhythm induced by Concurrent Excitation and Inhibition," by A. Forbes. "Factors in Rhythmic Activity of the Nervous System," by T. Graham Brown.

— Chemical, 8.30. "Azo-dyestuffs of the Triphenylmethane Group," by A. G. Green and R. N. Sen. "Aniline Black and Allied Compounds," by A. G. Green and A. E. Woodhead. "Action of Grignard's Reagents on Esters of Dibasic Acids," by J. T. Hewitt and D. B. Steinberg. "Chemical Examination of the Bark of *Euonymus atropurpureus*," by H. Rogerson. "Constitution of Aminotyrosine and the Action of Oxidases on some Tyrosine Derivatives," by C. Funk. "Fuane 2:5-Di-Aldehyde," by W. F. Cooper and W. H. Nuttall. "Dynamic Isomerism of Ammonium Thiocyanate and Thiocarbamide," by W. R. G. Atkins and E. A. Werner. "The Distillation and Densities of Mixtures of Allyl Alcohol and Water," by T. A. Wallace and W. R. G. Atkins. "A Modification of the Beckmann Apparatus by which Constant Readings are obtained in Determining the Boiling-points of Aqueous Solutions," by E. Knecht and J. P. Batey.

FRIDAY, 17th.—Royal Institution, 9. "High Frequency Currents," by W. Duddell, F.R.S.

SATURDAY, 18th.—Royal Institution, 3. "Interpretation in Song," by H. Plunkett Greene.

## TO CORRESPONDENTS.

Dr. E. W. Prevost.—Dr. C. A. Doremus, of New York, is desirous of communicating with Dr. E. W. Prevost, whose address he has mislaid.



# THE CHEMICAL NEWS.

VOL. CV., No. 2738.

## THE VOLATILITY OF METALS OF THE PLATINUM GROUP.\*

By Sir WILLIAM CROOKES, O.M., For. Sec. R.S.

For the last two years I have been using an electric furnace, and some facts which came under my notice on the occasion of a break-down of the heating arrangement led me to suspect that platinum was not so entirely fixed at temperatures well below its melting-point as has been universally accepted by chemists and physicists.

The electric resistance furnace used (Fig. 1) is on the Heraeus system. It consists of a highly refractory porcelain tube, around which is coiled a ribbon of platinum foil, 11 mm. wide, 2.8 metres long, and 0.01 mm. thick, each convolution almost, but not quite, touching its neighbour. The ribbon closely enwraps the tube, practically covering the surface to be heated, so that the heat produced by the passage of

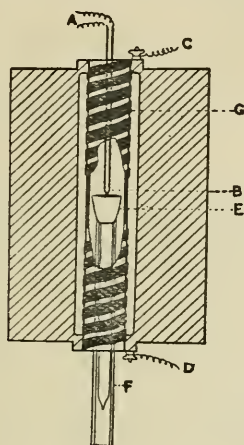


FIG. 1.

- A, Wires from thermo-junction.
- B, Platinum-platinum-rhodium junction.
- C, D, Terminals of platinum strip.
- E, Crucible.
- F, Porcelain supporting tube.
- G, Platinum strip.

the electric current is immediately transmitted to the tube. The tube is 4 cm. internal diameter; the object to be heated stands on a porcelain rod fixed upright in the middle of the tube. The body of the furnace is made to slide up and down by means of a windlass, so as to allow the crucible to be properly adjusted. The temperature of the furnace is measured by a Le Chatelier platinum and platinum-rhodium thermo-couple.

Although the melting-point of platinum is 1753° (Waidner and Burgess, *Bulletin of the Bureau of Standards, Washington*, 1907, vol. iii., p. 208) it is not safe to use the furnace at higher temperatures than about 1500°, as a temporary variation in the voltage of the current for a few minutes, or a reduction of the resistance, may easily make a difference of one or two hundred degrees.

After a certain time the platinum ribbon coil gets thinner and melts at the weakest part, and the furnace becomes useless until a new porcelain tube and platinum ribbon coil are supplied. During the two years I have had the furnace in use this breakdown has happened three times.

\* A Paper read before the Royal Society, March 7, 1912.

On examining the point of rupture I was struck by the appearance of a fine glistening dust on the porcelain tube. I carefully removed particles to the slide of a microscope, and found the dust to consist of beautifully formed hexagonal plates with a brilliant metallic lustre and perfect crystalline form. The amount at my disposal was infinitesimal—not more than a few milligrammes—and careful chemical examination showed me that the crystals were almost entirely platinum. A control examination by Messrs. Johnson and Matthey confirmed my observation. When the furnace was taken to pieces more crystalline deposits of platinum were found, especially inside the outer tube facing the platinum spiral. Fig. 2 shows some of these crystals.

At first sight it might seem superfluous to try experiments to see if platinum volatilised at all when strongly heated, considering how many generations of chemists have been daily igniting and weighing platinum crucibles. But it is customary among chemists to cleanse their crucibles between each using, and in some cases they are scoured with fine sand. It therefore seemed of interest to subject a platinum crucible to a temperature approaching that to which the platinum resistance coil had been exposed. As an appreciable amount of platinum had sublimed and deposited in the form of crystals in the furnace it was possible that a carefully weighed platinum

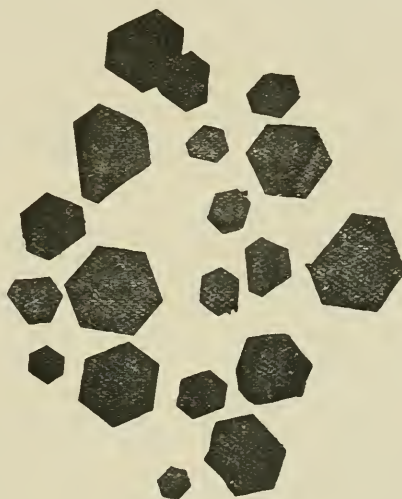


FIG. 2.

crucible exposed to a high temperature, after a certain number of hours, might show a detectable diminution in weight.

I assumed that the loss of weight in a platinum crucible by sublimation, at temperatures not much above those available in chemical laboratories, would be very small, and would require the balance to be in the best condition to enable its indications to be relied on. The balance—a very delicate chemical one—I employed for this research was put into accurate adjustment, and not used for any other purpose. It was kept in a dry room at nearly constant temperature, and was locked when not actually in use. The grain\* weights used were made for me in 1864 by Johnson and Matthey, and were turned out of bars of melted, cast, and well hammered platinum. They were adjusted by the method I described in the *CHEMICAL NEWS* for April 19, 1867, and *Phil. Trans. Roy. Soc.*, 1873, p. 288, and have been in use ever since.

\* My results are given in grains, not grammes. I have used my standard platinum grain weights for nearly fifty years, and they are too valuable to discard in favour of gramme weights, which would demand many months' work on them to bring them to the state of accuracy into which I have now got the grain weights.

In 1895 Mr. Chaney, Superintendent of Weights and Measures, tested my 1000-grain platinum weight against their absolute standards, with the result that it was shown to be 3.9858 grains light. This made no difference to previous work with the weights, as in chemical operations the object is not to ascertain the *absolute* weight of a substance in terms of a grain or gramme, but to determine its *relative* weight in comparison with that which it possessed at some other time before submission to certain analytical or synthetical operations. If the weighings are performed with the same weights it does not matter whether they are absolutely of the value they profess to be—but it is of vital importance that they should bear a known proportion to each other.

On receiving Mr. Chaney's result I adjusted the 1000 grain weight by melting a bead of pure gold on it of the exact weight required, viz., 3.9858 grains, and then re-adjusted the whole series in the same way so as to get them *absolutely* as well as *relatively* accurate. In 1897 the readjustment being complete I again asked Mr. Chaney to tell me the absolute weight of my platinum 1000 grains, and he returned it in a few days, saying that *in air*, at 62° F. and pressure of 30 inches, my 1000 grain weight weighed 999.99574 grains, and *in vacuo* it weighed 999.90300 grains. Comparisons made last year showed that their values have remained absolutely unaltered, and I have the satisfaction of knowing they are as near perfection as can reasonably be expected.

By taking all precautions and using Gauss's method of interchanges, the balance will clearly indicate a difference of 0.0001 of a grain when loaded with 1000 grains in each pan. In the course of the research it was seen that this extreme delicacy was not needed, and as weighing to such minute accuracy is very tedious, I have not, as a rule, gone beyond three places of decimals.

#### Platinum at 1300°.

A platinum crucible in good condition was ignited, cooled in a desiccator, and, an hour after, transferred to the balance. It weighed 150.487 grains. It was put into the electric furnace at 1300° C., and kept at that temperature for two hours. It was then removed, allowed to cool in a desiccator, and after another hour in the balance room it was found to weigh 150.458 grains, showing a loss of no less than 0.029 grain.

It was now put into the furnace for another two hours, and the temperature kept at 1300° (a white heat). On cooling an hour in the balance case its weight was found to be 150.427 grains.

The following table shows the losses by sublimation when exposed to a temperature of 1300° for two hours at a time—being cooled and weighed between each heating:—

TABLE I.

|                                | Grains. | Loss.         | Per cent |
|--------------------------------|---------|---------------|----------|
| Original weight of platinum .. | 150.487 | —             | —        |
| After 2 hrs. at 1300°, weighed | 150.458 | 0.029 = 0.019 |          |
| " 4 "                          | 150.427 | 0.060 = 0.040 |          |
| " 6 "                          | 150.394 | 0.093 = 0.062 |          |
| " 8 "                          | 150.365 | 0.122 = 0.081 |          |
| " 10 "                         | 150.344 | 0.143 = 0.095 |          |
| " 12 "                         | 150.316 | 0.171 = 0.114 |          |
| " 14 "                         | 150.295 | 0.192 = 0.128 |          |
| " 16 "                         | 150.266 | 0.221 = 0.147 |          |
| " 18 "                         | 150.233 | 0.254 = 0.169 |          |
| " 20 "                         | 150.209 | 0.278 = 0.185 |          |
| " 22 "                         | 150.194 | 0.293 = 0.195 |          |
| " 24 "                         | 150.180 | 0.307 = 0.204 |          |
| " 26 "                         | 150.159 | 0.328 = 0.218 |          |
| " 28 "                         | 150.140 | 0.347 = 0.231 |          |
| " 30 "                         | 150.118 | 0.369 = 0.245 |          |

These results are shown plotted as a curve in Fig. 3.

After this heating, and loss of 0.245 per cent of its weight, the platinum crucible was not appreciably different in appearance from the time it was first put into the electric furnace. I examined its surface under the microscope,

expecting to find the re-crystallisation described by Mr. Rosenheim (*Roy. Soc. Proc.*, lxx., 252). I was unable to detect any appearance resembling the photograph given in his paper. Probably the heating in his case was extended much beyond the thirty hours to which my crucible was exposed.

The action known as "air washing" (particles from a white-hot semi-molten surface being mechanically carried

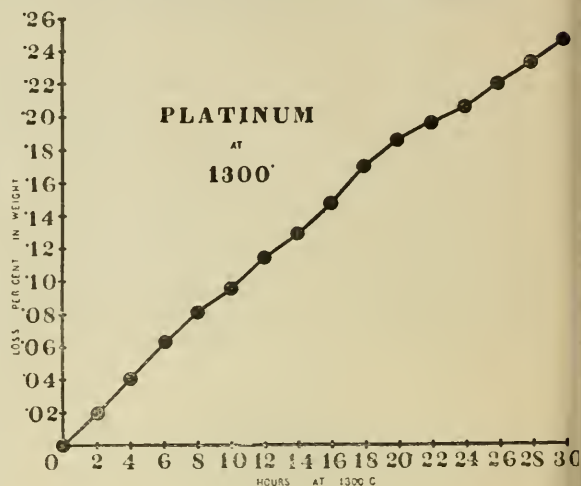


Fig. 3.

away by a current of impinging air), could not be active in the case of this experiment, for the tube of the furnace was closed at the top, nearly closed at the place where the crucible stood, and almost completely obstructed at the lower end. Therefore the platinum was in almost perfectly still air.

#### Palladium at 1300°.

Having with platinum obtained such unexpected results I tested palladium in similar conditions. The metal used was pure, in the form of thick plate, bright and polished on both sides.

In the following table it will be seen that, like platinum, palladium loses weight when exposed to a temperature of 1300° for two hours at a time, cooling and weighing at each interval:—

TABLE II.

|                                 | Grains. | Loss.         | Per cent. |
|---------------------------------|---------|---------------|-----------|
| Original weight of palladium .. | 58.007  | —             | —         |
| After 2 hrs. at 1300°, weighed  | 57.939  | 0.068 = 0.117 |           |
| " 4 "                           | 57.883  | 0.124 = 0.214 |           |
| " 6 "                           | 57.825  | 0.182 = 0.314 |           |
| " 8 "                           | 57.808  | 0.199 = 0.343 |           |
| " 10 "                          | 57.761  | 0.246 = 0.424 |           |
| " 12 "                          | 57.735  | 0.272 = 0.469 |           |
| " 14 "                          | 57.720  | 0.287 = 0.495 |           |
| " 16 "                          | 57.702  | 0.305 = 0.526 |           |
| " 18 "                          | 57.674  | 0.333 = 0.574 |           |
| " 20 "                          | 57.656  | 0.351 = 0.605 |           |
| " 22 "                          | 57.642  | 0.365 = 0.629 |           |
| " 24 "                          | 57.624  | 0.383 = 0.660 |           |
| " 26 "                          | 57.607  | 0.400 = 0.690 |           |
| " 28 "                          | 57.591  | 0.416 = 0.717 |           |
| " 30 "                          | 57.575  | 0.432 = 0.745 |           |

The curve plotted from these data is shown in Fig. 4.

Moissan (*Comptes Rendus*, cxliii., January 22nd, 1906) says that "palladium is more easily fused than platinum, but is apparently less volatile." From the foregoing data it appears that at temperatures much below its melting-point palladium is three times as volatile as platinum.

At the end of the series the plate of metal had curved into an arc of about 60°, and its concave surface showed



raised blisters. These blisters appeared after the first few heatings, and were due evidently to the liberation of occluded gas; further heating did not seem to increase the blisters. On examining the plotted curve the two-hourly loss of weight is seen to be greater in the earlier stages, diminishing up to ten hours, and then pretty regular in a straight line. This agrees with the supposition that gas was given off during the earlier heatings, and the extra loss at these stages was due to the weight of gas liberated. From the above data the loss due to occluded gas would be about 0.15 of a grain, and supposing it were hydrogen it would measure about 111 cc.

The bulk of 58 grains of palladium would be about 0.34 cc., and as palladium will absorb more than 600 times

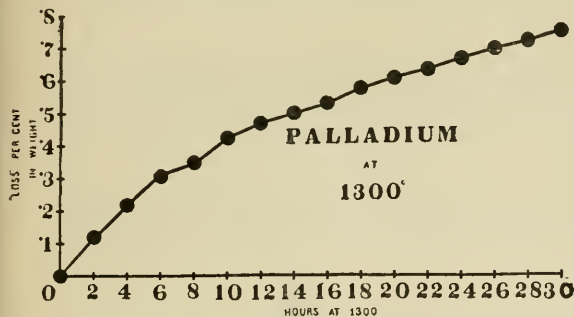


FIG. 4.

its volume of hydrogen, the amount it could have held is 204 cc.

As the heatings at 1300° progressed there was a gradual change in the surface of the metal from smooth to crystalline, and at the end of the thirty hours the surface had a crystalline moiré appearance, similar to that shown by iridium after similar heating, but not so marked, the crystals being smaller. The metallic appearance was unimpaired and no oxidation was detected on the surface.

#### Iridium at 1300°.

In May, 1908 (*Roy. Soc. Proc.*, A, lxxx., 535), I suggested to chemists the great advantages of using crucibles of pure iridium instead of platinum in laboratory work. An iridium crucible is hard as steel; it may be heated for hours

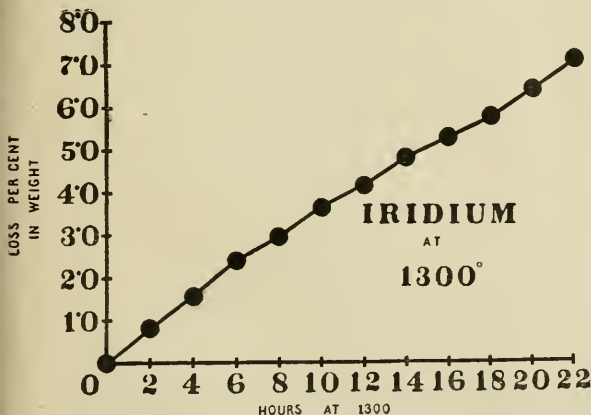


FIG. 5.

over a smoky Bunsen burner without injury. It will stand hours of boiling in aqua regia without appreciable attack; lead and zinc can be melted in it and boiled at a full red-heat; likewise nickel, copper, gold, and iron can be melted in an iridium crucible, and poured out without injury. I

used an iridium crucible for more than a year in the scandium research, and did not notice any appreciable diminution in weight. Any slight loss I attributed to mechanical abrasion during the cleaning and burnishing with sand sometimes rendered necessary after an experiment.

Subsequent observations, however, led me to suspect that iridium was not altogether fixed at high temperatures; looking into the literature of the subject I met with several references to the supposed volatility of this metal.

Accordingly, I commenced experiments to see if I could detect loss of weight in iridium at 1300°, a temperature at which I had found platinum to be slightly volatile.

An iridium crucible was heated for a few minutes in the electric furnace, and then cooled in a desiccator. It was taken to the balance room, put near the balance for an hour, and then placed on the pan. In an hour's time it was weighed and found to be 145.726 grains. This therefore was taken as the original weight from which to calculate the loss, if any, after long exposure to the high temperature of the furnace.

The crucible was put into the hot electric furnace, standing on an iridium plate, and kept at 1300° for two hours. It was then removed, allowed to cool with all precautions, when its weight was found to be 144.520 grains, showing a loss of 1.206 grains or about 0.8 per cent. The experiment was repeated until the iridium had been exposed to this temperature for a total of twenty-two hours.

The following table shows how in the above circumstances iridium loses weight, the data being plotted as a curve in Fig. 5:—

TABLE III.

|                                | Grains. | Loss.  | Per cent. |
|--------------------------------|---------|--------|-----------|
| Original weight of iridium ..  | 145.726 | —      | —         |
| After 2 hrs. at 1300°, weighed | 144.520 | 1.206  | = 0.828   |
| " 4 "                          | 143.430 | 2.296  | = 1.576   |
| " 6 "                          | 142.208 | 3.518  | = 2.414   |
| " 8 "                          | 141.379 | 4.347  | = 2.983   |
| " 10 "                         | 140.354 | 5.372  | = 3.686   |
| " 12 "                         | 139.577 | 6.149  | = 4.220   |
| " 14 "                         | 138.605 | 7.121  | = 4.887   |
| " 16 "                         | 137.878 | 7.848  | = 5.385   |
| " 18 "                         | 137.151 | 8.575  | = 5.884   |
| " 20 "                         | 136.151 | 9.575  | = 6.571   |
| " 22 "                         | 135.092 | 10.634 | = 7.297   |

Before the crucible was exposed to long continued heating to 1300° it was bright and polished. After four hours' heating it had a slightly crystalline look, which increased each time until after twenty-two hours the surface had assumed a beautiful moiré appearance.

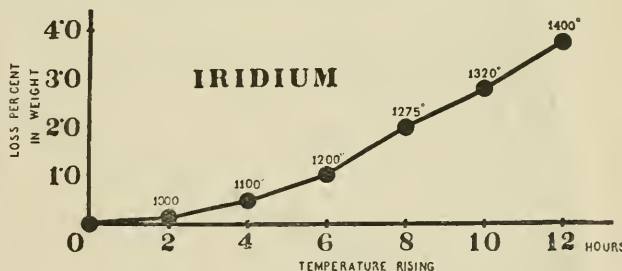


FIG. 6.

After the iridium crucible had been heated in the electric furnace in the above experiments until it had lost 7.297 per cent of its weight, it was submitted to further experiment to see if loss of weight was proportional to the temperature. After the last experiment at 1300° the crucible was exposed for two hours at a time to temperatures rising from 1000° to 1400°, with the following results:—

TABLE IV.

|                                   | Grains. | Loss. | Percent. |
|-----------------------------------|---------|-------|----------|
| Weight of iridium at starting ..  | 135.092 | —     | —        |
| After 2 hours at 1000° ..         | 134.927 | 0.165 | = 0.122  |
| After 2 additional hours at 1100° | 134.509 | 0.583 | = 0.432  |
| " " " 1200°                       | 133.746 | 1.346 | = 0.996  |
| " " " 1275°                       | 132.395 | 2.697 | = 1.996  |
| " " " 1320°                       | 131.367 | 3.725 | = 2.757  |
| " " " 1400°                       | 129.996 | 5.096 | = 3.772  |

The curve, Fig. 6, is plotted from the above data, and shows conclusively that the loss of weight for equal periods of time is proportional to the temperature.

After this severe treatment the crucible, which had taken on a crystalline appearance over the whole surface when the series commenced, began to show approaching disintegration along its edges, and after several more heatings of two hours pieces began to crumble when touched with the forceps.

The disintegration of iridium has been examined by Messrs. Holborn and Austin (*Phil. Mag.*, Series 6, vol. vii., p. 388), who found that at high temperatures (1670°) a narrow strip disintegrated about ten times as rapidly in the air as platinum.

#### Rhodium at 1300°.

I next tried rhodium, a metal intermediate in fusibility between platinum and iridium, and similar to iridium in its resistance to chemical agents which attack platinum. In my paper above quoted (*Roy. Soc. Proc.*, A, lxxx., 535) I suggested the use of rhodium for crucibles in the laboratory. Its low density (11 as against iridium 22) would be a great advantage in quantitative operations, as the weight of a rhodium crucible would be only half that of one made of platinum, and its cost would not be excessive.

The following table shows the losses in weight when metallic rhodium is exposed to a temperature of 1300° for two hours at a time for thirty hours in an electric furnace; the rhodium being cooled and weighed at intervals of two hours:—

TABLE V.

|                                 | Grains. | Loss. | Per cent. |
|---------------------------------|---------|-------|-----------|
| Original weight of rhodium ..   | 32.774  | —     | —         |
| After 4 hours at 1300°, weighed | 32.767  | 0.007 | = 0.021   |
| " 6 " " "                       | 32.765  | 0.009 | = 0.027   |
| " 8 " " "                       | 32.763  | 0.011 | = 0.034   |
| " 10 " " "                      | 32.760  | 0.014 | = 0.043   |
| " 12 " " "                      | 32.758  | 0.016 | = 0.049   |
| " 14 " " "                      | 32.755  | 0.019 | = 0.058   |
| " 16 " " "                      | 32.752  | 0.022 | = 0.067   |
| " 18 " " "                      | 32.749  | 0.025 | = 0.076   |
| " 20 " " "                      | 32.746  | 0.028 | = 0.085   |
| " 22 " " "                      | 32.743  | 0.031 | = 0.095   |
| " 24 " " "                      | 32.739  | 0.035 | = 0.107   |
| " 28 " " "                      | 32.734  | 0.040 | = 0.122   |
| " 30 " " "                      | 32.731  | 0.043 | = 0.131   |

Fig. 7 shows the curve plotted from these data.

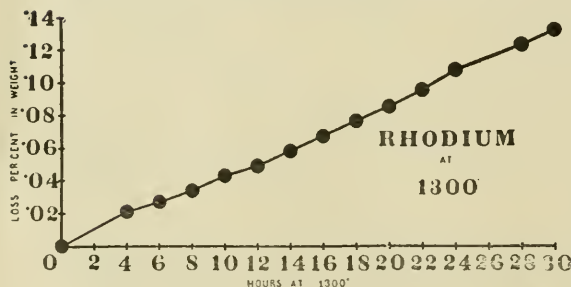


FIG. 7.

After the above heating the rhodium did not appear much changed. It was a little darker, as if with a slight tarnish, but showed no crystalline structure.

#### Ruthenium at 1300°.

Ruthenium does not lend itself to such experiments as the foregoing owing to the formation of a volatile oxide. A piece of the pure metal, in the form of a highly polished plate, exposed in the furnace to a temperature of 1300° for eight hours, lost 25 per cent of its weight.

After this heating the ruthenium was of a dull black and was covered with a coating of oxide having a fused appearance.

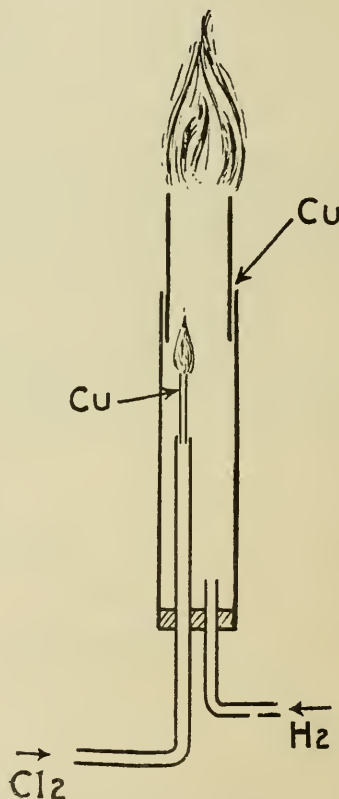
(To be continued)

## A FLAME EXPERIMENT.

By ALFRED C. EGERTON.

THE following experiment was devised to illustrate that in the different cones of a flame different chemical actions are occurring. The idea consisted in making two flames, in each of which a single chemical action occurs, and then introducing into each of them some substance which would make visible the different chemical actions that are taking place.

A glass cylinder (6" x 0.75") is fitted with a cork at the lower end, through which pass a glass tube, ending three-quarters of the way up the cylinder, and also another



shorter glass tube. The upper end of the outer glass cylinder and of the longer inner tube have copper foil fitted inside and projecting out 1 inch from the end of the glass; the spring of the foil keeps it in position, and a large and small copper nozzle is thus obtained. The longer inner tube is connected with an aspirator filled with chlorine, and the shorter one to a cylinder of hydrogen. The hydrogen is turned on and lit at the top of the wider cylindrical tube. The copper foil, when it warms up,



colours the flame green. The chlorine is then turned on gently, and it lights itself at the lower nozzle quite safely; the copper makes the small flame intensely blue.

Two flames are thus obtained, the lower one shows the action  $H + Cl = HCl$ , the copper chloride produced making the flame brilliantly blue, and visibly illustrating the action; while the upper large flame consists of the action  $H_2 + O = H_2O$ , which is made visible on the outside of the flame by the green colour produced by the vapourised copper. The hydrogen should be well turned on; the stream of chlorine should be turned out first, and then the pure green of the copper in the oxyhydrogen flame is seen more distinctly. The experiment is easy to carry out, and is rather a striking one for a lecture.

R.M.A., Woolwich.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

Ordinary Meeting, May 2nd, 1912.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"Petrifactions of the Earliest European Angiosperms." By MARIE C. STOPES, D.Sc.

"Distribution of Oxydases in the Plant and their Role in the Formation of Pigment." By F. KEEBLE, D.Sc., and E. F. ARMSTRONG, Ph.D., D.Sc.

The methods of investigation in general use do not admit of the determination in detail of the distribution of oxydases in the tissues of plants and animals. Hence the hypothesis that pigments are produced by the action of oxydases in colourless chromogens, though rendered probable by recent researches, cannot be regarded as established.

Methods are now described which allow of the macroscopic and microscopic recognition of plant oxydases. By the application of these methods it is shown that in the Chinese primrose (*Primula sinensis*) the distribution of oxydases in the tissues coincides with that of the pigments of the flower and other parts of the plant. Thus, the hypothesis with respect to the rôle of oxydases in pigment-formation receives confirmation.

It is proved that *P. sinensis* contains two peroxydases which differ from one another in their chemical reactions and in their localisation.

Both peroxydases occur in the root, stem, leaves, and also in the flower. One is associated with the epidermal and subjacent layers; another with the tissues of the vascular bundles. Both epidermal and bundle peroxydase contribute to the formation of pigment in the petals of the flower.

In certain varieties of *P. sinensis* the tissues of stem and flower give a direct oxydase reaction. By the use of races of *P. sinensis* of known genetical constitutions the nature of the inhibition which results in the formation of Dominant white flowers has been determined. In such flowers the capacity for forming pigment exists, but pigment-formation is arrested by an inhibitor, whereas, when tested in the ordinary way, flowers of Dominant white *P. sinensis* give no peroxydase reaction; they yield a marked reaction with a peroxydase reagent after preliminary treatment with hydrogen cyanide or carbon-dioxide.

Thus it is proved definitely that Dominant whites contain a substance which inhibits, but does not destroy, peroxydase. Experiments with Recessive white flowers, the genetical behaviour of which indicates that they lack either peroxydase or chromogen, show that they contain peroxydase. Inasmuch as Recessive whites contain no inhibitor of oxydase, failure to form pigment is to be attributed to lack of chromogen.

The distribution of peroxydases in *P. sinensis* is to be regarded as typical of that in flowering plants generally, and the method appears to be capable of wide application in the study of the distribution of oxydases.

"Manifestation of Active Resistance to the Growth of Implanted Cancer." By B. R. G. RUSSELL, M.D., Imperial Cancer Research Fund.

"Nature of the Immune Reaction to Transplanted Cancer in the Rat." By WM. H. WOGLOM, M.D., Imperial Cancer Research Fund.

"The Instability of a Cortical Point." By T. GRAHAM BROWN and C. S. SHERRINGTON, M.D., F.R.S.

"Measurement of Trypanosoma rhodesiense." By J. W. W. STEPHENS, M.D., D.P.H., and H. B. FANTHAM, D.Sc., B.A.

### CHEMICAL SOCIETY.

Ordinary Meeting, April 18th, 1912.

Prof. PERCY F. FRANKLAND, LL.D., F.R.S., President, in the Chair.

(Concluded from p. 226).

80. "Molecular-weight Determinations from the Relative Lowering of the Vapour Pressure of Ethereal Solutions." By ROBERT WRIGHT.

By the following method the chief difficulties of molecular weight determination from the relative lowering of the vapour pressure of solutions have been to some extent avoided.

Two small flasks of about 100 cc. capacity are connected by means of mercury-sealed stoppers to a differential manometer of the form shown. The height of the whole apparatus is about 60 cm., the bulb on the stem below the U-tube is of 15 cc. capacity, and the length of stem below the mercury-sealed vacuum tap is about 30 cm., the height of the cylinder being 15 cm.

In a molecular-weight determination, one of the flasks marked in a suitable manner is fitted with a stopper, and weighed. Next 2—4 grms. of solute are introduced, and its weight determined. Both flasks are now three-quarters filled with ether, and connected with the apparatus, the tap being left open, and the whole is clamped in position over the cylinder of mercury.

By means of beakers of hot water the ether in both flasks is alternately boiled and allowed to cool, the cooling being accelerated by immersing the flasks in cold water. Three such boilings are usually sufficient to sweep all air out of the apparatus; the ether should now fill from a quarter to a third of each flask; care should be taken that none of the solute crystallises out. The outsides of the flasks are now dried, and the mercury allowed to mount in the gauge. As soon as the mercury has risen so as to occupy half the bulb, the ether which has condensed on the surface of the rising column is driven back into the flasks by gently heating the bulb with a small flame. It is advisable during this part of the operation to warm gently all that part of the gauge which is above the bulb.

The whole apparatus is now placed in a glass-fronted cupboard, and left for three or four hours, so that it may cool to the temperature of the room. Both flasks are now gently tapped so as to shake their contents, and ten minutes later the difference in height of the mercury columns read by means of a cathetometer. This difference—which should be about 3 cm.—is the lowering of the vapour pressure due to the solute. In order to disconnect the flasks, the apparatus is raised until the end of the gauge is only about 1 cm. below the surface of the mercury in the cylinder; the flasks are then, if necessary, gently warmed with the hand until the mercury in the manometer is depressed so as to occupy a level below the tap, which is then closed, and the whole apparatus lifted free from the cylinder. On opening the tap, air is admitted to the

flasks, and the one containing the solution is disconnected, stoppered, and weighed, and by this means the weight of the ether obtained.

The molecular weight of the solute is now calculated from the formula:—

$$\frac{f-f'}{f'} = \frac{W/M}{w/m},$$

where  $f$  and  $f'$  are the vapour pressures of solvent and solution,  $W$  and  $M$  the mass and molecular weight of the solute, and  $w$  and  $m$  those of the solvent.

The value of  $f$ , the vapour pressure of the pure solvent, is best obtained by noting the temperature of the experi-



ment and consulting a table of vapour pressures, interpolating, if necessary, by means of the usual logarithmic rule. This avoids errors due to impurities in the ether, which will not affect the differential value  $f-f'$ .

The following are a few typical results; in general it will be seen that the errors are less than 10 per cent:—

|                    | M.W. found. | True M.W. |
|--------------------|-------------|-----------|
| Nitrobenzene . . . | 129         | 123       |
| Azobenzene . . .   | 190         | 182       |
| Benzoic acid . . . | 112         | 122       |
| Aniline . . .      | 98          | 93        |
| Naphthalene . . .  | 135         | 128       |

As the object of the experiments was not a research on vapour pressures, but a simple method of determining molecular weights, no great care was taken to obtain perfectly pure reagents. The ether was the methylated variety which had been washed and re-distilled, and the solutes purified in the usual manner gave sharp melting or boiling-points.

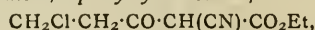
The stoppers used were of capillary rubber tubing, a substance not altogether suitable owing to the solubility of ether in it; but as the only effect of this solubility is the removal of some ether from the solution, the use of rubber does not materially affect the results.

(We are indebted to the Chemical Society for permission to reproduce the accompanying illustration).

89. "Condensation of Acid Chlorides with the Ethyl Esters of (a) Cyanoacetic Acid, (b) Malonic Acid, and (c) Acetoacetic Acid." (Preliminary Note). By CHARLES WEIZMANN, HAROLD DAVIES, and HENRY STEPHEN.

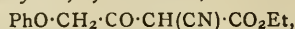
The following condensation products have been prepared with the view of using them for the preparation of amino-ketones and their derivatives:—

*Ethyl β-Chloropropionylcyanoacetate*,



prepared from β-chloropropionyl chloride and ethyl sodio-cyanoacetate, crystallises from a mixture of benzene and light petroleum, and melts at 68°; it gives a copper compound melting at 159°.

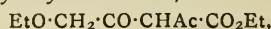
*Ethyl phenoxyacetylcyanoacetate*,



prepared from phenoxyacetyl chloride and ethyl sodio-cyanoacetate, yields a copper compound melting at 191°. The free condensation product prepared from this copper compound crystallises from light petroleum, and melts at 44°.

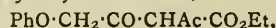
*Ethyl ethoxyacetylmalonate*,  $\text{EtO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}(\text{CO}_2\text{Et})_2$ , obtained from ethoxyacetyl chloride and ethyl sodiomalonate in dry benzene, is an oil boiling at 165°/19 mm.

*Ethyl ethoxyacetylacetoacetate*,



prepared from ethoxyacetyl chloride and ethyl sodioacetoacetate in dry benzene, is best purified by means of the copper compound. It boils at 132–133°/12 mm.

*Ethyl phenoxyacetylacetoacetate*,



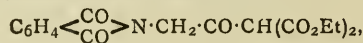
obtained by condensing phenoxyacetyl chloride and ethyl sodioacetoacetate, is a solid melting at 85–86°. It is best purified through the copper compound, and gives the ferric chloride reaction.

*Ethyl amyloxyacetylacetoacetate*,



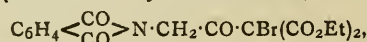
prepared from sodium acetoacetate and amyloxyacetyl chloride, is a liquid boiling at 176°/14 mm.

*Ethyl phthaliminoacetylmalonate*,



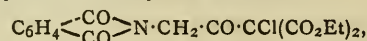
obtained from phthalylglycyl chloride and ethyl sodiomalonate in dry benzene, is a white solid, which crystallises from alcohol and melts at 68°. When submitted to steam distillation in presence of dilute sulphuric acid, it yields phthaliminoacetone (m. p. 124°). The residue, an oil insoluble in sodium carbonate, yields, on crystallisation from alcohol, ethyl phthaliminoacetoacetate (m. p. 119°), identical with the compound described by Gabriel and Colman (*Ber.*, 1909, xlii., 1244). This substance does not give a coloration with ferric chloride, but when its alcoholic solution is mixed with a solution containing an equimolecular quantity of potassium ethoxide in alcohol, a crystalline potassium compound is obtained, which, when dissolved in water and decomposed with cold dilute acetic acid, yields the enolic modification of *ethyl phthaliminoacetoacetate*, melting at 70°, and gives a purple coloration with ferric chloride.

*Ethyl phthaliminoacetylchloromalonate*,



is obtained when ethyl phthaliminoacetylmalonate is treated with a 20 per cent solution of bromine in chloroform. It crystallises from methyl alcohol in colourless needles melting at 123°.

*Ethyl phthaliminoacetylchloromalonate*,

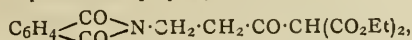


prepared by heating phthalylglycyl chloride with the potassium compound of ethyl chloromalonate in dry benzene,



crystallises from methyl alcohol in colourless needles, melting at 99°. On distillation in a current of steam in presence of dilute sulphuric acid, it yields phthaliminoacetic acid.

Ethyl  $\beta$ -phthaliminopropionylmalonate,



obtained in a manner similar to that described in the preparation of ethyl phthaliminoacetylmalonate, crystallises from methyl alcohol in needles melting at 62°.

$\beta$ -Phthaliminopropionic acid,



was obtained by hydrolysis of the corresponding amyl ester by means of concentrated hydrobromic acid at 40°.

Amyl  $\beta$ -phthaliminopropionate is easily obtained by heating molecular quantities of potassium phthalimide and amyl  $\beta$ -chloropropionate. It melts at 56°, and distils at 220°/12 mm. without decomposition.

91. "The Combustion of Carbon." By THOMAS FREDERIC RHEAD and RICHARD VERNON WHEELER.

Work by previous experimenters regarding the first reaction that takes place when carbon burns in oxygen was discussed.

The alternatives are:—

- (a)  $\text{C} + \text{O}_2 = \text{CO}_2$ , followed by
- (b)  $\text{CO}_2 + \text{C} = 2\text{CO}$ ;

and—

- (c)  $2\text{C} + \text{O}_2 = 2\text{CO}$ , followed by
- (d)  $2\text{CO} + \text{O}_2 = 2\text{CO}_2$ .

The authors attempted to obtain evidence as to which reaction is most likely to take precedence at different temperatures, by determining the relative velocities of the above reactions under the same experimental conditions.

The results obtained showed (1) that some carbon monoxide is produced during the oxidation of carbon at low temperatures, under conditions which do not admit of the reduction of carbon dioxide by carbon. On the other hand, (2), carbon dioxide is produced at low temperatures in quantity which cannot be altogether accounted for by the supposition that carbon monoxide is first formed, and then oxidised to carbon dioxide.

When carbon is burned at low temperatures, therefore, carbon dioxide and carbon monoxide are produced simultaneously.

An account of experiments made to discover the nature of the reaction responsible for this simultaneous production of the two oxides was reserved for a future communication.

92. "The Use of Phenolphthalein as an Indicator. The Slow Rate of Neutralisation of Carbonic Acid." By JAMES WILLIAM McBEAN.

It was shown that titrations with phenolphthalein as indicator require about ten minutes for the end-point to be attained, even in the absence of a gaseous space. This is not due to changes in the phenolphthalein, for these are not appreciable during many months in very low concentration of alkali (about  $0.7 \times 10^{-6}$  N-OH'). The phenomenon has been traced to the presence of carbon dioxide (carbonate), which is always intentionally or unintentionally present. It is uncertain which is the slow reaction, the rate of hydration of dissolved carbon dioxide, or the rate of electrolytic dissociation of the carbonic acid.

Carbon dioxide affects the amount of phenolphthalein necessary to produce maximum depth of colour, but it also affects enormously the amount of acid or alkali required to change the colour of the end-point by a definite amount.

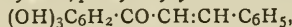
The very pale colour obtained at a concentration of OH' = about  $0.7 \times 10^{-6}$  was shown to be the most sensitive colour for the end-point, and permanent colour standards were described which identify this region. It was recommended that in titrating, before either of the liquids to be titrated are placed in the titration vessel, the water in the

latter should be coloured to the position of the final end-point with phenolphthalein and alkali.

93. "Some Hydroxy-ketonic Dyes." By JATINDRA MOHAN DUTTA and EDWIN ROY WATSON.

On account of their resemblance to the flavones and butein, the following compounds have been prepared:—

2 : 3 : 4-Trihydroxyphenyl styryl ketone,—



obtained by the condensation of cinnamic acid and pyrogallol with zinc chloride, forms chocolate-coloured plate-like crystals, melting at 125—126°.

2 : 3 : 4-Trihydroxyphenyl benzylmethyl ketone,  $(\text{OH})_3\text{C}_6\text{H}_2 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_5$ , prepared by condensing  $\beta$ -phenylpropionic acid and pyrogallol, crystallises in light pink prismatic crystals, melting at 86—87°.

2 : 3 : 4-Trihydroxyphenyl 2'-hydroxystyryl ketone,  $(\text{OH})_3\text{C}_6\text{H}_2 \cdot \text{CO} \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , prepared from *o*-hydroxycinnamic acid and pyrogallol, melts at 170°.

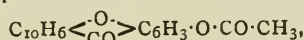
2 : 4-Dihydroxyphenyl 2'-hydroxystyryl ketone,  $(\text{OH})_2\text{C}_6\text{H}_3 \cdot \text{CO} \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , prepared from *o*-hydroxycinnamic acid and resorcinol, melts at 124—126°.

2 : 4-Dihydroxyphenyl 2'-hydroxynaphthyl ketone,  $(\text{OH})_2\text{C}_6\text{H}_3 \cdot \text{CO} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OH}$ , prepared from  $\beta$ -naphthol-carboxylic acid and resorcinol, forms brown plate-like crystals melting at 204—206°.

The monoacetyl derivative of dihydroxynaphthaxanthone,

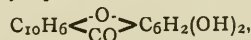
$\text{C}_{10}\text{H}_6 \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{C}_6\text{H}_2(\text{OH}) \cdot \text{O} \cdot \text{CO} \cdot \text{CH}_3$ , prepared by boiling 2 : 3 : 4-trihydroxyphenyl 2'-hydroxynaphthyl ketone with acetic anhydride and a trace of pyridine, melts at 200°.

Acetoxynaphthaxanthone,—



prepared similarly from 2 : 4-dihydroxyphenyl 2'-hydroxynaphthyl ketone, forms cream-coloured needle-shaped crystals melting at 217°.

3 : 4-Dihydroxynaphthaxanthone,—



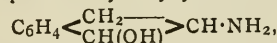
prepared by heating 2 : 3 : 4-trihydroxyphenyl 2'-hydroxynaphthyl ketone in a sealed tube with water, and also by the hydrolysis of its monoacetyl derivative, forms small plate-like crystals, melting at 280—285°.

Hydroxynaphthaxanthone,  $\text{C}_{10}\text{H}_6 \begin{array}{c} \text{O} \\ \diagup \quad \diagdown \\ \text{CO} \end{array} \text{C}_6\text{H}_3 \cdot \text{OH}$ , prepared by the hydrolysis of acetoxynaphthaxanthone, forms needle-shaped crystals which do not melt at 285°.

The dyeing properties of some of the above compounds were described.

94. "The Externally Compensated and Optically Active Hydroxyhydrindamines, their Salts and Derivatives." By WILLIAM JACKSON POPE and JOHN READ.

Methods were given for the preparation in quantity of externally compensated hydroxyhydrindamine,—



and for the resolution of this base into its optically active components by means of *d*- $\alpha$ -bromocamphor- $\pi$ -sulphonic acid. The rotation constants of the *d*- and *l*-hydroxyhydrindamines and the number of their salts and derivatives have been determined.

95. "The Four Stereoisomeric Optically Active 2 : 4-Dimethyltetrahydroquinolines." By JOHN THOMAS.

The molecule of 2 : 4-dimethyltetrahydroquinoline contains two asymmetric carbon atoms, and the synthetic product, obtained by the reduction of 2 : 4-dimethylquinoline, should therefore be resolvable into four optically active isomerides. The four isomerides in question can be isolated from the synthetic base by crystallisation with the *d*- and *l*- $\alpha$ -bromocamphor- $\pi$ -sulphonic acids.

96. "The Optical Activity of Salts and Derivatives of *d*-Camphor- $\beta$ -sulphonic Acid." By JOSEPH IVON GRAHAM.

For the purpose of ascertaining to what extent the molecular rotatory powers are dependent on concentration, the optical rotations (at constant temperature) of a number of salts of *d*-camphor- $\beta$ -sulphonic acid in aqueous solution have been determined for the mercury green, mercury-yellow, and sodium D-lines. In the case of the zinc, cadmium, and magnesium salts, no appreciable change in rotatory power is observed on increasing the concentration, whilst the barium, calcium, and copper salts show a diminution of rotatory power, and the ammonium and piperidine salts show an increase of rotatory power under similar conditions. On the other hand, no change in rotatory dispersion is produced by varying the concentration of the salts.

It is concluded that these changes cannot be dependent on variation of degree of electrolytic dissociation alone, but depend principally on the character of the metallic atom or electro-positive group. The "piperido-lactone" of this acid is now proved to be the piperidine salt.

The rotation constants of other derivatives, for example, the chloride, piperide, and the anhydramide, in chloroform solution have also been determined, and the influence of change of constitution on rotatory dispersion is illustrated in the case of the anhydramide in which the nitrogen atom has become linked to the carbon of the carbonyl group.

97. "Some Mixed Phosphonium Derivatives." By WILLIAM JACKSON POPE and CHARLES STANLEY GIBSON.

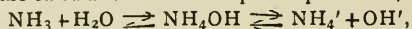
The authors described the preparation of phenyl-*p*-tolylmethylallylphosphonium and phenyl-*p*-tolylbenzylmethylphosphonium compounds and related substances; they were unable to resolve these compounds, which contain an asymmetric quivalent phosphorus atom, into optically active components.

98. "The Alkaloidal Salts of Phenylmethylphosphinic Acid." By WILLIAM JACKSON POPE and CHARLES STANLEY GIBSON.

Salts of phenylmethylphosphinic acid,  $\text{CH}_3(\text{C}_6\text{H}_5)\text{P}(\text{O})\text{OH}$ , with *l*-menthylamine, cinchonine, cinchonidine, quinine, and *l*-hydroxyhydrindamine have been prepared and submitted to careful fractional crystallisation without evidence of resolution being obtained. It thus appears that phenylmethylphosphinic acid is not resolvable into optically active components.

99. "The State of Ammonia in Aqueous Solution." By THOMAS FIELD WINMILL.

For the calculation of the complete equilibrium,—



it is necessary to know the "apparent dissociation constant" of ammonia, and also the partition-coefficient between water and an indifferent solvent at three temperatures. The necessary measurements have been made for ammonia, mono-, di-, and tri-methylamine, mono-, di-, and tri-ethylamine, and mono-, di-, and tri-propylamine at 18°, 25°, and 32°35'.

100. "The Absorption Spectra of some Metallic Solutions." By Sir WALTER NOEL HARTLEY.

Konrad Schaefer has investigated the absorption spectra of nitrates (*Zeitsch. wiss. Photochem.*, 1910, viii., 212), and whilst confirming the author's observations in all particulars (*Trans.*, 1902, lxxxi., 556; 1903, lxxxiii., 221), has somewhat extended them.

Prior to the publication of this paper in 1903, the author had examined thin layers of molten potassium nitrate 0.5 mm. in thickness, but found no selective absorption. The absorption spectra of metallic nitrates and of alkyl nitrates, the former in the state of solution and solid (Schaefer), the latter both as liquid, as solution in alcohol, and as vapour, are indisputable evidence that the bands of absorption in the former belong to the salt molecule, and that as under no condition do the alkyl nitrates exhibit such selective absorption, their constitution must be essentially different. The effect of solution on the absorption spectra of different nitrates (with the author's explana-

tion Schaefer does not agree) are explained on the view that they are not ionised.

101. "The Absorption Spectra of Permanganates." By Sir WALTER NOEL HARTLEY.

J. E. Purvis has examined the influence of dilution on the colour and the absorption spectra of various permanganates (*Proc. Camb. Phil. Soc.*, 1909, xv., 111), but his views, based on ionisation, do not satisfactorily explain the changes observed. A simpler explanation is offered similar to that given in the case of nitrates which form basic salts, and in particular thorium nitrate. A similar change takes place in manganese nitrate and in manganese sulphate. In the latter salt a transient absorption band which is feeble becomes a continuous absorption, and is evidently caused by the oxidation of the salt in solution. It indicates the progress of a chemical reaction, and the band disappears when the reaction is completed.

## PHYSICAL SOCIETY.

Ordinary Meeting, April 26th, 1912.

Mr. A. CAMPBELL, B.A., Vice-President, in the Chair.

THE adjourned discussion on Mr. H. Donaldson's paper on "The Coefficients of Expansion of Fused Silica and Mercury" was resumed.

Prof. H. L. CALLENDAR opened the discussion by communicating a paper "On the Expansion of Vitreous Silica."

Prof. Callendar begged leave to reintroduce to the notice of members the method and apparatus for the investigation of the expansion of vitreous silica which he had described and demonstrated at a meeting of the Society on March 22, 1901. The late Mr. A. W. Shenstone, whose work as the pioneer of vitreous silica was so well known, had on that occasion kindly provided him with two rods of the material 1.5 mm. in diameter and 40 cm. long, and also with a tube 1 cm. diameter and 30 cm. long. The rods were electrically heated in a very thin and uniform platinum tube 3 mm. in diameter, the resistance and expansion of which had previously been investigated with great care in connection with some experiments on the effusion and transpiration of gases at high temperatures. The method possessed special advantages for work at high temperatures because the rod could be raised to any desired temperature not exceeding 1700° C. in three or four minutes with little or no disturbance of the surrounding conditions, and the mean temperature could be inferred with considerable accuracy either from the expansion or the resistance of the platinum tube. The preliminary results of the investigation were published by Mr. Shenstone in his lecture on Vitreous Quartz at the Royal Institution, on March 8-1901. The final results, communicated to the Physical Society on March 22, 1901, were reported in the *CHEMICAL NEWS* of March 29th, and other papers, but were not considered to be of sufficient importance to merit more extended publication at that time. In view, however, of various misunderstandings which had arisen, and of the increased interest taken in the question at the present time, it might be worth while to give a brief summary of the old results. The expansion was found to be accurately reversible up to 900° C. with a nearly uniform coefficient, approximately  $0.58 \times 10^{-6}$  between 300° C. and 900° C. There was a well marked flat or change-point in the curve near 1000° C. above which the slope resumed its original value as far as 1400° C. When maintained at a steady temperature in this region the rod showed a continuous increase of length accompanied by marked superficial devitrification. In order to separate the permanent elongation due to this cause from the reversible expansion, a variable zero method was adopted. The current was switched off immediately after each reading at high temperatures, and the zero



observed as soon as the apparatus had cooled to atmospheric temperature. The contraction gave the reversible effect, the difference of the zeros before and after, the permanent elongation. The latter change was found to occur more rapidly as the temperature was increased. Above  $1400^{\circ}\text{C}$ . a reversible contraction was observed, which was demonstrated at the meeting on a greatly magnified scale by means of an optical lever. After repeated heatings to  $1600^{\circ}\text{C}$ . or  $1700^{\circ}\text{C}$ . the change-point at  $1000^{\circ}\text{C}$ . disappeared, and the expansion became more uniform, but the devitrification had by this time proceeded so far that the material would be valueless if annealed in this way. Further heating soon caused the alteration to extend in places through the core of the rod, which became very brittle and broke. The reversible expansion had by this time increased to nearly double its original value. The second rod similarly tested showed precisely similar effects, but the heating in this case was not pushed beyond the stage of superficial devitrification. The results differed widely from those previously obtained by Le Chatelier by comparison with a porcelain rod (probably owing to uncertainties in the expansion of porcelain), but had since been verified over the range  $0^{\circ}\text{C}$ . to  $1000^{\circ}\text{C}$ . by the observations of Holborn and Henning, and of Randall. The material appeared to be eminently suitable for accurate work at temperatures up to  $800^{\circ}\text{C}$ . or  $900^{\circ}\text{C}$ ., but its irreversible elongation and devitrification at higher temperatures rendered it useless for high-temperature gas thermometry, which was the primary object of the investigation.

More recently the expansion of vitreous silica at ordinary temperatures had acquired special interest in connection with mercurial thermometry, and standards of length and expansion. The majority of observers had used the Fizeau method with specimens 10 mm. to 15 mm. long. Somewhat different values had been found for different specimens with different standards of comparison. For a cylindrical specimen on a platinum-iridium tripod Chappuis found  $50 \times 10^{-6}$  for the expansion from  $0^{\circ}\text{C}$ . to  $100^{\circ}\text{C}$ ., and  $0.385 \times 10^{-6}$  for the coefficient at  $0^{\circ}\text{C}$ . Scheel, for a similar specimen, tested against a quartz-crystal ring, found  $45.5 \times 10^{-6}$  from  $0^{\circ}\text{C}$ . to  $100^{\circ}\text{C}$ ., and  $0.217 \times 10^{-6}$  at  $0^{\circ}\text{C}$ . For a ring specimen tested in a vacuum by the absolute method he found values almost identical with Chappuis; but Randall, employing a similar ring specimen, also made by Zeiss, found the mean coefficient from  $16^{\circ}\text{C}$ . to  $80^{\circ}\text{C}$ . (which is nearly the same as that from  $0^{\circ}\text{C}$ . to  $100^{\circ}\text{C}$ .) to be only  $0.424 \times 10^{-6}$ . Such differences might be due to accidental errors, or to differences in form and treatment of the specimens employed, or to differences in the standards of comparison. But since the whole expansion of 1 cm. of fused silica between  $0^{\circ}\text{C}$ . and  $100^{\circ}\text{C}$ . was only of the order of one wave-length of light, it was also possible that small constant errors might arise in so delicate an experiment from gas-films or other surface effects variable with temperature. It seemed therefore desirable to measure the expansion of the long silica rods at low temperatures by a direct interference method in which such sources of error were excluded.

The free end of the silica rod in the platinum tube apparatus was accordingly fitted with a small lens giving Newton's rings with a fixed lens. An expansion of  $50 \times 10^{-6}$  with this arrangement would give about fifty rings, which could be easily counted in two or three minutes by suitably regulating the electric heating. The fractions of a half wave-length could be estimated with great precision by measuring the diameters of the first and last rings. The experiment was so easy that an error of the order of 1 per cent appeared to be practically impossible, and an accuracy of 1 in 1000 might reasonably be expected. The ring system itself was not exposed to changes of temperature, and the method was absolute in the sense that the result did not depend on assuming the expansion of some other material. This method gave a smaller and more rapidly diminishing value for the expansion of the silica rods than that obtained by other observers

employing the orthodox Fizeau method with short specimens. On the other hand, Donaldson's relative comparisons of a silica metre over the range  $0^{\circ}\text{C}$ . to  $30^{\circ}\text{C}$ . with three metre standards of invar, nickel, and nickel-steel respectively (the expansion of which relative to the platinum-iridium standard has been determined at the Bureau International) gave results the mean of which agreed closely with Chappuis' formula, in which the expansion of platinum-iridium was also assumed. It would appear either that different specimens of silica differed in expansion or that the discrepancies were due to errors in the absolute determinations, which were of a higher order of difficulty than the relative comparisons.

The recent determinations of the relative expansion of mercury in silica bulbs by Harlow and Eumorfopoulos agreed well with that of Chappuis obtained with a *verre dur* bulb, when Chappuis' values of the expansion of silica and *verre dur* were assumed, but gave somewhat lower values for the expansion of silica and *verre dur*, when the values of Callendar and Moss for the absolute expansion of mercury were assumed, and the cubical coefficient was taken as three times the linear. This introduced the further question as to whether the expansion of silica or *verre dur* could be assumed to be isotropic since neither could be perfectly annealed. In order to elucidate this point he had designed an arrangement for observing by the Fizeau method the differential expansion between a tripod and a ring cut from the same tube. The finished apparatus was expected in a day or two, and might be expected to afford some positive evidence on the subject. It was proposed to examine different specimens of glass as well as silica to see if any relation could be traced between the residual strains and the expansion, and whether differences could be eliminated by annealing. If his own observations of the expansion of silica and mercury were correct, the difference between the radial and axial expansion of a silica tube should be small in absolute magnitude, but not beyond the limits of sensitiveness and accuracy of the differential method. The absolute measurement of a linear coefficient was a difficult and delicate operation, and any errors were increased threefold in deducing the cubical coefficient; but in the case of a material like silica, where the expansion was so small as to minimise the importance of exact measurement of temperature, the weight thermometer method afforded a most valuable check on the accuracy of the hydrostatic method, provided that the isotropy of the bulb employed were independently verified. It might even prove to be more accurate than the hydrostatic method at low temperatures, where the latter suffered from increased viscosity lag and other difficulties of manipulation.

#### DISCUSSION.

Mr. F. J. HARLOW quoted some observations on the apparent expansion of mercury and silica from  $0^{\circ}\text{C}$ . to  $44^{\circ}\text{C}$ . that he had recently made. These gave a still lower value for the expansion of silica.

Dr. G. W. C. KAYE congratulated Mr. Donaldson on drawing from Prof. Callendar such an interesting account as they had just listened to. He was glad Prof. Callendar was taking up such an important subject, as the question of the expansion of silica was now an international one.

Dr. J. A. HARKER stated that Prof. Callendar suggested that Donaldson's coefficient for the expansion of silica ultimately depended upon the coefficient found for a small specimen of platinum-iridium found by the Fizeau method. The metre rods against which Mr. Donaldson had compared his silica metre had had their coefficients determined at the Bureau International relatively to their standard platinum-iridium metre, but this had had its coefficient determined absolutely, as well as by the Fizeau method.

Mr. H. DONALDSON, in reply, said that Prof. Callendar had raised several questions to which it was difficult to give any answer at the present time. He suggested that different specimens of silica might behave differently. Their standard metre bars had been compared against the standard platinum-iridium bar at the Bureau International

but this had had its coefficient of expansion determined absolutely and not relatively. Mr. Sears and himself had also designed a method of finding the difference between the longitudinal and transverse coefficients of drawn silica by means of an optical lever method. He valued Prof. Callendar's remarks on the difficulty of annealing silica.

*Note added by Prof. Callendar.*—With the assistance of Mr. A. Eagle, he had made some observations on the difference between the radial and axial expansion of a silica tube similar to that from which the bulbs of the mercury weight thermometers employed by Harlow and Eumorfopoulos had been constructed. The tube had been supplied by the Silica Syndicate, and the tripod and ring had been optically worked by Messrs. Hilger. Three sets of determinations had been made by Mr. Eagle on three different days with closely concordant results. The mean of these showed that the axial coefficient of expansion of the specimen tested exceeded the radial coefficient by  $0.20 \times 10^{-6}$  over the range  $18^\circ \text{C. to } 90^\circ \text{C.}$  This result agreed as closely as could be expected with the values of the cubical coefficient deduced from the weight thermometer observations of Harlow and Eumorfopoulos when the values of Callendar and Moss for the absolute expansion of mercury were assumed.

A paper on "The Solution of Network Problems by Determinants" was read by Mr. R. APLEYARD.

The paper is a practical application of the method described before the Physical Society in 1885 by Dr. J. A. Fleming.

Let it be supposed that cyclic currents have been assigned to all the meshes of a given network, and that all capacities (K, in farads), inductances (L, in henries), and leakances (S, in mhos) have been converted into resistances in ohms ( $\frac{1}{Kip}$ ,  $Lip$ ,  $\frac{1}{S}$ , where  $p = 4\pi\omega$ ). The general network problem, then, is to find the current, in amperes, in any given branch, corresponding to the application of an E.M.F. of sine form, between any two fixed points in the network. The procedure for solving such a problem may be summarised as follows:—

1. Denote the cyclic current in the mesh on one side of the given branch by, say,  $(X+Y)$ , and the cyclic current in the mesh on the other side of it by, say, Y, so that X is magnitude of the real current through the given branch.

2. Number the meshes in consecutive order, beginning at the generator mesh and ending at the  $(X+Y)$  mesh. Let the Y mesh be next to the last.

3. Write down successively the total resistance of each mesh in the order of their numbers—including capacities, inductances, and leakances, converted into resistances as above—and make these values the successive terms of the leading diagonal of a determinant, beginning at the top. Observe that the order of the columns of the determinant is now the same as the order of the meshes. So also is the order of the rows.

4. To fill up any given row (or column), say, the  $n$ th, observe what are the resistances of the branches crossed in passing from the  $n$ th mesh successively to the 1st, 2nd, 3rd . . . mesh, and make these values the respective constituents of the 1st, 2nd, 3rd . . . places in the  $n$ th row. The  $n$ th constituent of the  $n$ th row will always be in the leading diagonal, and it is to be given a plus sign. All constituents outside the leading diagonal are to be given a minus sign.

5. Now replace the  $(X+Y)$  and (Y) columns of the determinant so formed by columns corresponding only to X and Y. To do this, add the  $(X+Y)$  column to the Y column to form a new Y column, and retain the  $(X+Y)$  column for a new X column. This is equivalent to multiplying out the fundamental mesh equations, and bringing all terms in X inside one bracket and all terms in Y inside another bracket. The final column now corresponds with X, and the penultimate column with Y. The determinant  $\Delta_n$  is thus completed.

6. Replace the final column by E, o, o, o, o . . . ,

putting E at the head of the column. Expand the determinant so formed, in terms of E, o, o, o, o . . . , and it becomes  $E\Delta_{n-1}$ . In general, this operation may be omitted, since  $\Delta_{n-1}$  can at once be written down when Operation 5 is completed.

7. Then by the well-known property of determinants,  $X = E \frac{\Delta_{n-1}}{\Delta_n}$ ; and the resistance  $r$ , between the two points of the network to which E is applied, is  $r = \frac{\Delta_n}{\Delta_{n-1}}$ .

8. If the network contains mutual inductances, a convention must be adopted in respect to signs. Regard each mutual inductance as a pair of parallel straight conductors; then a sudden increase of current in one conductor will induce in the other a momentary current in a direction opposed to that in the first. If this induced current is in the same direction as the cyclic current of the mesh to which the second conductor belongs, then the mutual inductance term  $Mip$  is to be regarded as plus, and if the induced current is in the opposite direction to that cyclic current,  $Mip$  is to be regarded as minus.

9. Observe that there can never be an M-term in the leading diagonal. There is, however, always an M-term in a constituent outside the leading diagonal, provided that the constituent corresponds to a mesh linked by mutual inductance to a mesh in which there is a varying current.

10. This method of solution is based upon the assumption of a sine-form E.M.F. of definite frequency, and consequently all the constants of the meshes are effective values corresponding to the selected frequency. If the conditions of equilibrium in any particular case do not explicitly contain a frequency term, the current wave may be of any shape; and under these circumstances the method applies to a current impulse of any form whatever.

#### DISCUSSION.

Mr. F. E. SMITH stated that current in one arm of a network due to an E.M.F. in another was the same as the current in the second arm caused by the same E.M.F. in the first arm.

The CHAIRMAN stated that Heaviside had investigated almost every possible bridge, with mutual and self-inductances in every arm. The method of determinants was undoubtedly very powerful, but he preferred the simple method of denoting the current in the various arms by unknown variables and then writing down equations for the potentials of the different points in the network. A mutual inductance could always have a plus or a minus sign. Thus for every bridge another could be obtained by connecting the mutual inductance up the other way. Frequently, however, this rendered it impossible to find a point of balance.

## NOTICES OF BOOKS.

*Theory of Sizing.* By HARRY NISBET. Manchester and London: Emmott and Co., Ltd. 1912.

THIS small book is one of the manuals issued by the "Textile Manufacturer," and contains a series of articles contributed by the author to that journal, some alterations having been made in them in order to make the book more suitable for use as a text-book or a work of reference. It discusses the general properties of the chief sizing ingredients and the factors which influence the selection of one or other of them for special purposes. Some size-mixing recipes are included, as well as many useful formulæ and data. Diagrams of the appearance under the microscope of the six chief varieties of starch are provided, and descriptions are given of the methods, both microscopical and chemical, which the author has found useful in identification of the starches.



*Rothamsted Experimental Station. Annual Report for 1911.* By A. D. HALL, Director. Harpenden: D. J. Jeffery. 1912.

THE Rothamsted Experimental Station occupies a unique position among institutions devoted to agricultural research, and no one who is interested in the science and practice of agriculture can afford to remain ignorant of the work which is being done at the station. The Annual Report for 1911 gives details of the yields of various crops for a year, which was, on the whole, very unfavourable from an agricultural point of view. Short abstracts of the papers published by the staff during the year are also included, and in the introduction a brief account is given of the objects, funds, and management of the station.

*Theoretical and Physical Chemistry.* By S. LAWRENCE BIGELOW, Ph.D. New York: The Century Co. 1912.

THIS book has been written for first-year college students who have attended a course of descriptive inorganic chemistry, with perhaps a little theory thrown in, but have no real grasp of the fundamental principles of the science. Very little mathematics is introduced, and the author has aimed at presenting the subject in the simplest way possible. His style is graphic, and the occasional colloquialism of his language will no doubt arrest the student's attention and perhaps make some impression on his memory, while the shortness of the paragraphs and the frequent use of heavy type for headings will be appreciated in revision. The references both to larger and more comprehensive text-books and to periodical literature are very full, and the average student will probably hardly find time to look them all up. Although in the main the text will give the student clear and accurate views of the outlines of theoretical chemistry, the author's statements are not always above criticism. For instance, there does not appear to be much justification for the use of the term "symbol weight" for "atomic weight," and it would be interesting to know who are the authors who use "combining weight" as synonymous with "atomic weight." Experienced teachers in this country will probably agree that it is perfectly easy to make quite clear even to young students the meanings of "atomic weight," "combining weight," and "equivalent weight," and they usually readily grasp the relations between them. Again, the author is hardly sound upon the subject of luminiferous ether, or at any rate it would be advisable to warn the student that his views are not those now generally accepted.

*Die Elektrochemischen Verfahren der Chemischen Gross-Industrie.* ("The Electrochemical Methods of the Chemical Major Industries"). Vol. II. By Dr. JEAN BILLITER. Halle-a.-S.: Wilhelm Knapp. 1911. (Mk. 28.50).

THE second volume of this work gives an account of the principles involved in methods of electrolysis in which no metal is precipitated and insoluble anodes are used, and the technical applications of these principles is discussed in detail. The electrolysis of water and electrolytic oxidations and reductions form the subject of the first chapter, both organic and inorganic compounds being taken into consideration. In the second chapter full information is given regarding the many processes involving the electrolysis of alkaline chloride solutions which are employed technically; the subject is very systematically treated, and the indexing of the book is excellent throughout. The preparation of bromine by the electrolysis of bromide solutions is included, and in an appendix the most recent discoveries and improvements of methods are briefly alluded to; this appendix refers to the subject matter of Part I. as well as Part II. As in the first volume, processes which seem to the author to be likely to be technically useful, but which have not yet been employed on a large scale, are occasionally described; and here he exhibits good judgment, and gives his readers every warrant for putting confidence in his views and predictions.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. cliv., No. 13, March 25, 1912.

**Hydrates of Zirconyl Chloride.**—Ed. Chauvenet.—Six different zirconyl chloride hydrates have been described, containing respectively 9, 8, 6.5, 4.5, and 3 molecules of water. The author has constructed the curve the coordinates of which are the heats of solution and the molecular weights of different mixtures of water and oxychloride, corresponding to all the possible hydrates. The points which correspond to mixtures containing 6.5, 4.5, and 3 H<sub>2</sub>O are exactly on straight lines, while the only angular points observed correspond to the products containing 2, 3.5, 6, and 8 H<sub>2</sub>O. Thus four definite hydrates of zirconyl chloride exist, viz., ZrOCl<sub>2</sub>.2H<sub>2</sub>O, ZrOCl<sub>2</sub>.3.5H<sub>2</sub>O, ZrOCl<sub>2</sub>.6H<sub>2</sub>O, and ZrOCl<sub>2</sub>.8H<sub>2</sub>O. The author has prepared specimens of these hydrates experimentally.

*Berichte der Deutschen Chemischen Gesellschaft,*  
Vol. xliv., No. 4, 1912.

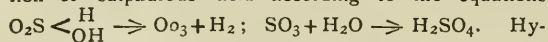
**Ultra-filtration in Analytical Chemistry.**—R. Zsigmondy, E. Wilke-Dörfurt, and A. v. Galecki.—A collodion membrane can conveniently be used for filtration in quantitative analysis. A precipitate dried on such a filter can very readily be completely detached from it, and many colloids can be directly filtered off. To prepare the membrane dilute commercial collodion solution containing ether is poured evenly on to glass, the ether is allowed to evaporate, and the whole is immersed in water; the collodion can then be peeled off. The perforated bottom of a porcelain funnel is covered with paper, the layer of collodion is placed upon it, and the two are made to adhere to the wall of the funnel by using a water pump.

**Quantitative Separation of Copper from Arsenic, Aluminium, Zinc, Tungsten, and Tin.**—Paul Jannasch and Oskar Rontala.—If to a solution of copper sulphate enough cane-sugar is added so that excess of soda produces no precipitate of copper hydroxide, H<sub>2</sub>O<sub>2</sub> produces in the solution a green coloration which changes on warming to blue. Finally a yellow precipitate, which gradually turns red, is separated. This precipitate is cuprous oxide, and the reactions are CuO + H<sub>2</sub>O<sub>2</sub> = CuH<sub>2</sub>O<sub>3</sub>, 2CuH<sub>2</sub>O<sub>3</sub> = Cu<sub>2</sub>O + 2H<sub>2</sub>O + 3O. Separate experiments will have to be performed in order to determine whether the cane-sugar undergoes any chemical change. The copper is quantitatively precipitated, and the method can be used to separate copper from arsenic, aluminium, zinc, tin, tungsten, &c.

**Humus Acid.**—Sven Odén.—The author has prepared an ammonium humate solution which is free from colloids, and also a suspension of humus acid which contains no inorganic salts. By measurements of the conductivity it may be proved that the action of NH<sub>4</sub>OH on humus acid is an instance of true salt formation. By neutralising humus acid with caustic soda it may be proved that the equivalent weight of humus acid is approximately 339. The acid is probably tribasic.

**Combustion of Carbon Monoxide.**—Heinrich Wieland.—In complete absence of the oxygen of the air carbon monoxide is converted into the dioxide in the cold by the action of water and palladium black. The first product of the reaction is formic acid, which is rapidly split up by the palladium into carbon dioxide and hydrogen. 
$$\text{O}:\text{C} < \overset{\text{OH}}{\text{H}} \rightarrow \text{CO}_2 + \text{H}_2$$
 The hydrogen is absorbed by the palladium. Apparently a similar reaction occurs at higher temperatures, and it may be shown that formic acid is formed.

Catalytic Conversion of Sulphur Dioxide into Sulphuric Acid.—Heinrich Wieland.—In absence of oxygen damp sulphur dioxide is converted by palladium black into sulphuric acid. The action must be a dehydration of sulphurous acid according to the equations



Hydrogen cannot be detected, but the palladium always contains sulphur, which is apparently formed by the reduction of the  $\text{SO}_2$ :  $\text{SO}_2 + 2\text{H}_2 = \text{S} + 2\text{H}_2\text{O}$ . It is known that in the sulphuric acid contact process the gases are not catalysed by platinum if they are perfectly dry, and apparently the action is not oxidation but dehydration.

## MISCELLANEOUS.

Royal Institution.—Prof. Poynting being unable to deliver his lectures at the Royal Institution on May 30 and June 6, the lectures on these dates will be given by Prof. C. G. Barkla, F.R.S., his subject being "X-Rays and Matter."

The University of Leeds.—Mr. R. A. Seymour-Jones, B.Sc.(Leeds), Diploma in Leather Manufacture, Leblanc Medal, 1910, who has been working as Research Assistant in the Department of Leather Industries of the University of Leeds since July, 1910, has obtained an appointment as Research Chemist in Messrs. Crosfield's Soap Works at Warrington.

Institute of Chemistry.—*Pass List, April Examinations, 1912.*—Of fifteen candidates who presented themselves for the Intermediate Examination, six passed: L. M. Clark; A. L. Davidson; F. C. Guthrie, B.A. (Cantab); J. T. Janson, B.Sc. (Lond.); T. S. Jones, B.Sc. (Lond.); and D. A. Legg. Of twenty-five candidates who presented themselves for the Final Examination, fifteen passed. In the Branch of Mineral Chemistry: A. M. Bailey; H. W. Gill, B.Sc. (Lond.); D. McDonald, B.Sc. (Lond.); A. H. Maude; and C. R. Robson. In the Branch of Physical Chemistry: F. W. Atack, B.Sc.Tech. (Manc.). In the Branch of Organic Chemistry: G. McL. Carruthers; R. B. Croad; J. R. Douglas, A.R.C.Sc.I.; A. J. Hale, B.Sc. (Lond.); D. Hamilton; J. Porter; and A. Rayner, B.Sc. (Lond.). In the Branch of the Chemistry of Food and Drugs, and of Water: L. E. Campbell, B.Sc. (Lond.); and E. Hill, A.R.C.Sc. (Lond.).

## MEETINGS FOR THE WEEK.

- MONDAY, 20th.—Royal Society of Arts, 8. (Howard Lecture). "Heavy Oil Engines," by Capt. H. R. Sankey, R.E.  
TUESDAY, 21st.—Royal Institution, 3. "The Study of Genetics," by Prof. W. Bateson, F.R.S.  
— Royal Society of Arts, 4.30. "Australian Railways," by the Hon. J. G. Jenkins.  
WEDNESDAY, 22nd.—Royal Society of Arts.—(Mr. Gordon Craig's absence from England will prevent his reading the paper on "The Art of the Theatre," announced for this date).  
THURSDAY, 23rd.—Royal Institution, 3. "Ice Formation in Canada," by Prof. Howard T. Barnes, F.R.S.  
— Royal Society. "Theory of a New Mechanism for Varying the Volume of Discharge in the Rotating Slider Crank Form in the Chamber Crank Chain of Rouleaux," by H. S. Hele-Shaw.  
"New Treatment of Optical Aberrations," by R. A. Sampson.  
"Extinction of Light by an Illuminated Retina," by Sir W. de W. Abney.  
"Optical Measurements at High Pressures," by W. Wahl.  
"Changes in certain Absorption Spectra in Different Solvents," by T. R. Merton.  
"Changes in Absorption Spectra of 'Didymium Salts,'" by W. C. Ball.  
"Viscosity of Carbon Dioxide," by P. Phillips.  
FRIDAY, 24th.—Royal Institution, 9. "Recent Advances in Agricultural Science," by A. D. Hall, F.R.S.  
SATURDAY, 25th.—Royal Institution, 3. "Interpretation in Song," by H. Plunkett Greene.

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# THE CHEMICAL NEWS.

VOL. CV., No. 2739.

## THE VOLATILITY OF METALS OF THE PLATINUM GROUP.\*

By Sir WILLIAM CROOKES, O.M., For.Sec.R.S.

(Concluded from p. 232).

THE diagram (Fig. 8) shows the loss per cent in weight of the metals platinum, palladium, iridium, rhodium, and ruthenium on the same scale when exposed to a temperature of  $1300^{\circ}$  for two-hourly periods.

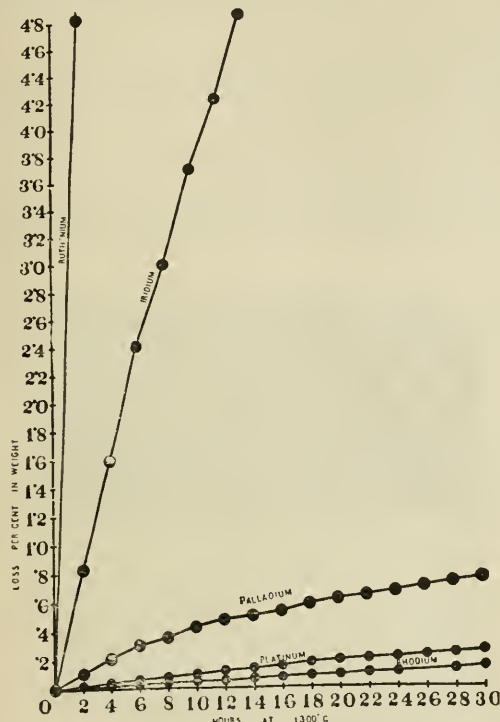


FIG. 8.

Having obtained such unexpected results at  $1300^{\circ}$  it was of interest to see how these metals would behave at a temperature sometimes employed in an analytical laboratory.

### Platinum at $900^{\circ}$ .

I therefore arranged a large Méker burner, with fused silica triangle and a surrounding clay cylinder to obstruct radiation, and with it heated an almost new platinum crucible. The thermo couple showed a temperature of about  $900^{\circ}$  in the centre of the hot crucible. After being heated to this temperature for ten minutes the crucible was cooled and transferred to the balance. It weighed 121.059 grains. It was now subjected to ten successive heatings of two hours each to  $900^{\circ}$ , weighing each time. The original weight of 121.059 grains was not found to vary in the slightest degree, and the same experiment tried with other platinum crucibles gave a similar result. A temperature of  $900^{\circ}$  is a full orange heat, and unless a blowpipe is used is higher than platinum crucibles are usually subjected to in the laboratory.

\* A Paper read before the Royal Society, March 7, 1912.

### Palladium at $900^{\circ}$ .

Palladium was next tried at a temperature of  $900^{\circ}$  under the same conditions to which platinum was subjected. The following table shows the diminution in weight:—

TABLE VI.

| Original weight of palladium             | Grains. | Loss.   | Per cent. |
|------------------------------------------|---------|---------|-----------|
| After 2 hours at $900^{\circ}$ , weighed | 56.579  | —       | —         |
| " 4 "                                    | 56.570  | 0.009 = | 0.0159    |
| " 6 "                                    | 56.560  | 0.019 = | 0.0336    |
| " 8 "                                    | 56.550  | 0.029 = | 0.0513    |
| " 10 "                                   | 56.535  | 0.044 = | 0.0778    |
| " 12 "                                   | 56.527  | 0.052 = | 0.0919    |
| " 14 "                                   | 56.521  | 0.058 = | 0.1025    |
| " 16 "                                   | 56.512  | 0.067 = | 0.1184    |
| " 18 "                                   | 56.505  | 0.074 = | 0.1308    |
| " 20 "                                   | 56.500  | 0.079 = | 0.1396    |
| " 22 "                                   | 56.491  | 0.088 = | 0.1555    |
| " 24 "                                   | 56.487  | 0.092 = | 0.1626    |
| " 26 "                                   | 56.481  | 0.098 = | 0.1732    |
| " 28 "                                   | 56.478  | 0.101 = | 0.1785    |
| " 30 "                                   | 56.477  | 0.102 = | 0.1803    |
| " 30 "                                   | 56.476  | 0.103 = | 0.1827    |

The palladium scarcely altered during these heatings. Beyond a faint pink tinge no signs of superficial oxidation could be detected, and the surface, with the exception of a few more blisters, presented practically the same appearance as it had after the  $1300^{\circ}$  series.

### Iridium at $900^{\circ}$ .

Having found platinum to be absolutely fixed at  $900^{\circ}$  it was of interest to see how iridium would behave at that temperature. Another iridium crucible was taken and its original weight, after good ignition, was found to be 175.374 grains. Heating to  $900^{\circ}$  over a Méker gas burner in air for two hours and twenty-five minutes reduced the weight to 175.322. In the following table are shown the gradual diminution in weight with the duration of heating:—

TABLE VII.

| Original weight of iridium . .              | Grains. | Loss.   | Per cent. |
|---------------------------------------------|---------|---------|-----------|
| After 2 h. 25 m. at $900^{\circ}$ , weighed | 175.374 | —       | —         |
| " 4 h. 40 m. "                              | 175.322 | 0.052 = | 0.030     |
| " 6 h. 40 m. "                              | 175.297 | 0.077 = | 0.044     |
| " 8 h. 40 m. "                              | 175.289 | 0.085 = | 0.048     |
| " 11 h. 40 m. "                             | 175.268 | 0.106 = | 0.060     |
| " 14 h. "                                   | 175.244 | 0.130 = | 0.074     |
| " 16 h. "                                   | 175.241 | 0.133 = | 0.076     |
| " 18 h. "                                   | 175.221 | 0.153 = | 0.087     |
| " 20 h. "                                   | 175.219 | 0.155 = | 0.088     |
| " 22 h. "                                   | 175.215 | 0.159 = | 0.091     |
| " 22 h. "                                   | 175.213 | 0.161 = | 0.092     |

After these successive heatings to  $900^{\circ}$ , the iridium crucible was a little darker than it was originally, but it had no crystalline moiré appearance, like the other one after having been heated for twenty-two hours to  $1300^{\circ}$ .

### Rhodium at $900^{\circ}$ .

Experiments were now instituted to see if a temperature of  $900^{\circ}$  continued for many hours would have any effect on metallic rhodium.

TABLE VIII.

| Original weight of rhodium . .           | Grains |
|------------------------------------------|--------|
| After 2 hours at $900^{\circ}$ , weighed | 32.731 |
| " 4 "                                    | 32.731 |
| " 6 "                                    | 32.731 |
| " 8 "                                    | 32.731 |
| " 10 "                                   | 32.732 |

The weight remains almost exactly the same. The differences, amounting to 0.001 grain, equal to a difference of 0.003 per cent, are due probably to slight superficial oxidation to  $\text{RhO}_2$  and reduction of the oxide to the metallic state in a reducing atmosphere.

I have plotted these curves on one diagram (Fig. 9) so that the volatility of the metals at  $900^{\circ}$  can be compared one with the other, and also with the corresponding curve of metals at  $1300^{\circ}$ . The horizontal scale of hours is the

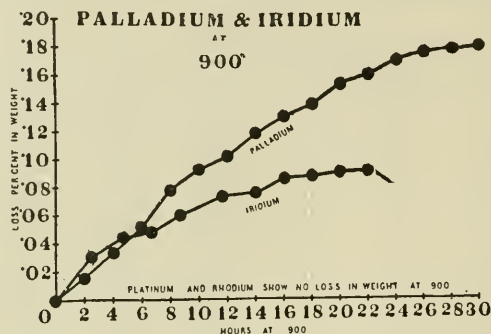


FIG. 7.

same in each, but to render the curves at  $900^{\circ}$  distinct I have been obliged to make the vertical scale of percentage loss ten times as large as it is in the  $1300^{\circ}$  curves.

#### Summary.

These results bear two explanations:—(1) The metal is volatile *per se* at these high temperatures, or (2) the metal unites with oxygen at a certain temperature, forming a volatile oxide, which may either volatilise unchanged, or may decompose at a higher temperature with deposition of the metal, the oxygen acting in this case as the temporary carrier of the metal. It is probable that each of these causes is active in one or other of the metals experimented with. I will take the case of the metal first tried, viz., platinum. The universal experience of chemists is against the supposition that platinum forms a volatile oxide below  $1300^{\circ}$ . Deville and Debray, who worked long and thoroughly on the platinum metals, agree that "platinum is distinguished from all the metals which accompany it in the mineral, by the fact that it does not unite direct with oxygen in whatever condition the two bodies are placed." (*Comptes Rendus*, 1878, vol. lxxvii., p. 441).

The mode of occurrence of the beautiful crystals of platinum is against the supposition that they are a product of the decomposition of an oxide, for the crystals deposit on a part of the apparatus that is at a slightly lower temperature than the bulk of the metal, and it is inconceivable that platinum should unite with oxygen to form a volatile oxide at one definite temperature, and part with this oxygen and come down in metallic crystals at a little lower temperature.

The boiling-point of platinum is put by Kaye and Laby at about  $2450^{\circ}$  ("Physical Constants," 1911, p. 49, Longmans). Moissan's electric furnace in which the arc is used is said by him to give with ease a temperature of  $3500^{\circ}$ , and here platinum enters into fusion in a few minutes, and soon volatilises. The metallic platinum collects in small brilliant globules and in powder on the cooler parts of the electrodes, or on the surface of the lower brick some centimetres from the crucible (Moissan, "Le Four Electrique," p. 43). No mention is made of the metal condensing in crystals.

I must therefore come to the conclusion that platinum is absolutely non-volatile at  $900^{\circ}$ , a temperature easily attainable in an analytical laboratory, and that the formation of crystals of the metal in the electric furnace is a true case of sublimation.

The next metal, iridium, under experiment behaves differently to platinum. It is admitted that iridium is volatile at a high temperature. Thus Mendenhall and Ingersoll (*Physical Review*, xxv., 13) speak of melting iridium into a globule and then remelting it two or three times before it entirely sublimed. This at a temperature above its

melting-point, which these authors put at between  $2300^{\circ}$  and  $2400^{\circ}$ .

Waidner and Burgess (*Bulletin of the Bureau of Standards*, Washington, vol. iii., p. 183) describing an "iridium furnace," of which the essential part is an iridium tube 25 cm. long, 2 cm. in diameter, and 0.25 mm. wall thickness, state that to avoid evaporation of the iridium it was coated with Nernst's refractory earth mixture.

These illustrations, however, are taken from observations of experimentalists who were working with iridium at or near its melting-point.

At high temperatures below  $1000^{\circ}$  iridium oxidises, forming an oxide,  $\text{Ir}_2\text{O}_3$ , which is volatile. Deville and Debray consider the alleged volatility of the metal is due to the formation of this volatile oxide. They say (*Comptes Rendus*, lxxvii., p. 445), "Above  $1000^{\circ}$  all volatilisation becomes impossible in our atmosphere, because the oxide of iridium ceases to exist, and the metal is at least as fixed as platinum."

In my experiments the cold iridium was put into the furnace previously heated to  $1300^{\circ}$  or thereabouts, and the metal quickly became hot. While it was rising to  $1000^{\circ}$  it oxidised superficially, and the oxide rapidly volatilised, accounting for the loss of weight.

I devised an experiment to see if iridium would volatilise at a high temperature in a vacuum.

A fused silica tube, 1 cm. diameter and 20 cm. long, had a bulb  $2\frac{1}{2}$  cm. diameter blown on the end (Fig. 10). In the bulb was put 27.619 grains of clean iridium, and the other

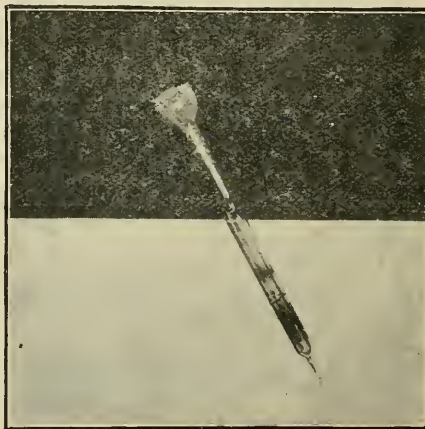


FIG. 10.

end of the silica tube was drawn out for connecting with the pump and sealing. It was exhausted to a high vacuum and heated to near redness along its whole length till all moisture and occluded gases had been removed; it was then sealed off.

The tube was placed bulb uppermost in the furnace in such a position that the iridium would be at the point of greatest heat, the lower part of the tube remaining comparatively cool. The bulb was kept at a temperature of  $1300^{\circ}$  for thirty hours. On examining the silica tube when cold it was seen that the long continued high temperature had caused the bulb and the upper part of the tube to devitrify, and become white and translucent and that it had an irregular black deposit on the lower part, which, on examination, proved to be metallic iridium.

The iridium removed from the bulb was now found to weigh 27.606 grains, showing a total loss of 0.019 grain or 0.069 per cent in thirty hours.

The presence of a deposit of iridium in the cooler end of the silica tube may thus be accounted for; during the heating of the bulb containing the iridium a little air



leaked in, and the oxide of iridium formed before the temperature became high enough to decompose it, volatilised and deposited on the cooler part of the tube. There the oxide remained until the heat rose to the decomposing-point—somewhere about  $1000^{\circ}$ .

I must not conclude this paper without expressing my thanks to the firm of Johnson and Matthey, to whom I am indebted for many specimens of the pure metals used in this research.

## THE ESTIMATION OF NITRITES IN POTABLE WATERS.

By G. D. ELSDON, B.Sc., A.I.C.

In a well-known English text-book on water analysis the following sentence occurs in connection with the estimation of nitrites by the starch-iodide method:—"Ferric salts also liberate iodine from potassium iodide when present in any quantity, but no potable water ever contains sufficient to produce the reaction."

Some little time ago the author had reason to doubt this statement on account of some peculiar results which he obtained when using the starch-iodide reagent, and some experiments were undertaken with a view to finding out what dilution of ferric iron would produce the "nitrite" reaction, when tested with starch and potassium iodide.

In order to do this standards were made up of various strengths of ferric iron, and these were then tested with starch and potassium iodide, the colours produced being matched with those obtained from solutions of sodium nitrite of known strengths treated in a similar manner. The method used was as follows:—Fifty cc. of the water to be tested were put into a Nessler glass and 1 cc. of roughly normal hydrochloric acid added, followed by 1 cc. of starch solution (0.5 per cent), and 1 cc. of potassium iodide solution (16 per cent)—it being necessary to observe this order. Proceeding in this way the following results were obtained:—

| Time for formation of colour. | Parts of ferric iron.* | Corresponding parts of nitrite.* |
|-------------------------------|------------------------|----------------------------------|
| 30 seconds                    | 1.0                    | 0.07                             |
| 3 minutes                     | 0.2                    | 0.03                             |
| 14 "                          | 0.1                    | 0.008                            |
| 35 "                          | 0.04                   | 0.002                            |
| 90 "                          | 0.02                   | 0.001                            |

From these results it will be seen that one part of ferric iron in fifty millions of water can just be detected by means of the starch-iodide test, whilst one part in ten millions gives quite an appreciable reaction.

As might be expected the same action takes place when ferric iron and nitrites are present together, as will be seen from the results given below. Standards were made up containing nitrites alone and nitrites with ferric iron; they were then treated with starch and potassium iodide in the usual manner.

| Nitrites present.* | Ferric iron present.* | Time for blue colour to appear. | Nitrites found.* |
|--------------------|-----------------------|---------------------------------|------------------|
| 0.00               | 0.00                  | 2.5 hours                       | 0.00             |
| 0.02               | 0.00                  | 180 seconds                     | 0.02             |
| 0.00               | 1.00                  | 30 "                            | 0.07             |
| 0.02               | 1.00                  | 20 "                            | 0.09             |

It will thus be seen that the interfering action of ferric iron is practically the same whether nitrites be present or not.

### The Action of Ferrous Iron.

It was found that when ferrous iron was present in solution, even in comparatively large amounts, in the

absence of nitrites, no action was produced on the starch-iodide reagent. Thus a solution containing ten parts of ferrous iron per million, and no nitrite, did not give the slightest blue colour in one hour. When, however, ferrous iron and nitrite were present together in solution it was found that the iron retarded the production of the blue colour by the nitrite, and therefore the nitrite was underestimated.

From these and similar experiments it was found that ferrous iron in quantities exceeding 0.1 per million causes a diminution in the blue colour produced by nitrites with the starch-iodide reagent. A few of the results are given below:—

| Parts of ferrous iron. | Parts nitrite present. | Parts nitrite found. |
|------------------------|------------------------|----------------------|
| 1.0                    | 0.02                   | 0.017                |
| 2.5                    | 0.02                   | 0.014                |
| 5.0                    | 0.02                   | 0.012                |
| 10.0                   | 0.02                   | 0.009                |
| 10.0                   | 0.01                   | 0.004                |
| 20.0                   | 0.02                   | 0.007                |
| 50.0                   | 0.02                   | 0.004                |

### The Griess-Ilosvay Test.

The effects of ferrous and ferric iron on the Griess-Ilosvay test were tried both in the presence and absence of nitrites. It was found that quantities of ferric iron varying from 0.01 to 1.5 parts per million produced no colour with the reagent, and, further, no colour was produced by ferrous iron in strengths varying from one to twenty parts per million. It was found also that ferrous and ferric iron did not affect the colour produced by nitrites.

The Griess-Ilosvay test is carried out as follows:—Fifty cc. of the water are placed in a Nessler glass, and 2 cc. of the reagent added. The colour produced is matched against similar glasses containing known amounts of nitrite. The reagent is made by heating 0.1 gm. of  $\alpha$ -naphthylamine with 20 cc. of glacial acetic acid, and when dissolved mixing the resulting solution with 130 cc. of roughly normal acetic acid; to this is then added 0.5 gm. of sulphanilic acid dissolved in 150 cc. of roughly normal acetic acid.

### Conclusions.

For the following reasons the author much prefers the Griess-Ilosvay reagent for testing for nitrites, both qualitatively and quantitatively:—

1. The colour is practically steady after standing about two hours, and it is easy to compare and match.
2. It is not affected by ferrous and ferric salts.
3. Only one solution has to be added, and this will keep for months without decomposition.

The starch-iodide test only seems to have one good point, namely, that the solutions required are ordinary laboratory reagents.

### The Significance of Nitrites in Potable Waters.

The authority cited at the beginning of this paper states that:—"Water containing a trace, however slight (of nitrite), must be regarded with grave suspicion unless some other source is found from which they have more probably been derived." It is quite obvious that the value of this remark depends entirely on the amount of nitrites which can be called "the slightest trace." The Griess-Ilosvay test is capable, with care, of detecting one part of nitrous nitrogen in a thousand millions of water (or even less), and no water has come under the author's notice which has not given a trace of colour with this reagent after standing four hours, not excluding several public supplies to which not the slightest suspicion can be attached. Few satisfactory waters have contained more than 0.005 parts of nitrous nitrogen per million, and none more than 0.01 per million. It seems probable, therefore, that a water would be entirely free from suspicion, as far as nitrites were concerned, if it contained less than 0.01 part of nitrous nitrogen per million.

\* All quantities of nitrite and iron given in this Paper are in parts per million, the parts of nitrite being calculated as nitrous nitrogen.

A NEW METHOD FOR THE DETERMINATION  
OF VANADIUM.

By D. J. DEMOREST.

THE following method for the determination of vanadium in steel depends upon the selective oxidation of ferrous sulphate in the presence of vanadyl sulphate by means of manganese dioxide. The vanadyl sulphate is then titrated by adding an excess of permanganate, the excess permanganate being titrated by sodium arsenite.

This differential oxidising action apparently contradicts the results of J. R. Cain (*Journ. Ind. Eng. Chem.*, 1911, iii., 476), who found that both iron and vanadium are oxidised, but the reasons for this discrepancy are shown in a note which will appear later.

The manganese dioxide should be sufficiently fine to pass through a 200-mesh sieve, and yet should settle in a beaker of water in thirty seconds.

The process in detail is as follows:—In a 500 cc. flask a 2-grm. sample of the steel or iron is dissolved in a mixture of 30 cc. of water and 12 cc. concentrated  $\text{H}_2\text{SO}_4$  with application of heat. Then 1 cc. of  $\text{HNO}_3$  (sp. gr. 1.42) is added cautiously to oxidise the iron, and the solution is boiled for a few minutes to remove the nitrous fumes. Then the solution is diluted with 30 cc. of water, and a strong solution of  $\text{KMnO}_4$  is added to completely oxidise all carbon, &c., and the solution is boiled. If the permanganate or the resulting  $\text{MnO}_2$  should disappear, not enough permanganate has been used, and more should be added. Now ferrous sulphate is added to reduce the  $\text{MnO}_2$ ,  $\text{HMnO}_4$ ,  $\text{H}_2\text{CrO}_4$ , and  $\text{H}_3\text{VO}_4$ , &c., and the solution is again boiled to remove any possible nitrous fumes. Then pure distilled water is added to make the volume about 250 cc.,  $\text{N}/10$   $\text{KMnO}_4$  added until the solution is pink, and the solution cooled to tap-water temperature. Ferrous sulphate solution is added until all reducible compounds, including chromic and vanadic acids, are reduced. Only enough ferrous sulphate should be added to be certain that there is a decided excess present. A solution, 1 cc. of which equals about 0.01 gm. of iron, is the one used. Now, about 1 gm. of chemically pure  $\text{MnO}_2$  is added, and the solution shaken vigorously. After two minutes a drop is tested with ferricyanide on a white plate to see if the iron is completely oxidised. It generally takes from four to six minutes. At the end of each minute the solution is tested for ferrous iron until none is present, and the shaking is continued for about one-half minute longer. It should be noted that a bluish colour will always be obtained in the presence of vanadyl sulphate after the test drop has stood for a few seconds. The end should be taken when the test does not show blue immediately. The blue colour which forms after a few seconds, even when there is no ferrous iron present, is due to the reduction of ferri- to ferrocyanide by the vanadyl sulphate. One can become familiar with this end by adding a drop of ferric sulphate containing vanadyl sulphate to a drop of ferricyanide on a white plate.

The  $\text{MnO}_2$  oxidises the ferrous sulphate to ferric sulphate, but does not oxidise the vanadyl sulphate,  $[\text{V}_2\text{O}_5(\text{SO}_4)_2]$ . Then the  $\text{MnO}_2$  is filtered off on an asbestos mat, using suction. From a burette a standard solution of  $\text{KMnO}_4$  is added until a pink tinge is present in the solution, and 1 cc. more is added, and after one minute the excess permanganate is titrated with  $\text{Na}_3\text{AsO}_3$  solution. The end-point is very sharp. If at this point the operator is not satisfied with this titration, the excess arsenite may be oxidised with  $\text{KMnO}_4$ , ferrous sulphate again added, then oxidised with  $\text{MnO}_2$  as before, and the titration repeated, thus giving a check on the titration. A blank determination must be run on a vanadium-free steel, and the result deducted. The blank generally amounts to about 0.00075 gm. V. The time required is about one-half hour, and the results are very satisfactory. In fact, the accuracy is about that of a phosphorus determination.

The vanadium steel standard furnished by the Bureau

Standards was analysed by the above method. The result of the Bureau chemists is 0.0143 per cent V and the average of the co-operating chemists is 0.15 per cent V. The writer obtains the following results, the average being 0.143 per cent:—

|       |       |
|-------|-------|
| 0.140 | 0.138 |
| 0.147 | 0.147 |
| 0.143 | 0.143 |

To further test the method, 2-grm. samples of vanadium-free steel with the addition of ferro-vanadium containing 0.00684 gm. of vanadium were analysed. The results were 0.00680 and 0.00690 gm. V. Another sample with 0.0342 gm. V was analysed, and 0.03432 gm. V was found.

To test the effect of chromium on the method, the Bureau of Standards' sample above mentioned was analysed with the addition of 0.100 gm. Cr. The results were 0.143 per cent and 0.143 per cent V, showing that chromium has no effect on the vanadium results. Scores of other determinations have been made, proving the accuracy of the method.

The  $\text{KMnO}_4$  solution used equals 0.001 gm. iron per cc., and the arsenite solution has the same strength. This makes the  $\text{KMnO}_4$  equal 0.000917 gm. vanadium per cc. The arsenite solution is made by dissolving about 2.25 grms.  $\text{As}_2\text{O}_3$  in  $\text{Na}_2\text{CO}_3$  solution and diluting to 2000 cc.—*Journal of Industrial and Engineering Chemistry*, iv., No. 4.

A COMBINED GOVERNOR AND GAUGE FOR  
MAINTAINING A REGULAR FLOW OF GAS,

AND A

THERMOSTAT WITH DELICATE ADJUSTMENT  
AND LONG RANGE.\*

By S. H. COLLINS, M.Sc.

IN the course of some investigations on the rate of evaporation of hydrocyanic acid gas from aqueous solutions, a regular flow of gas was required, and it became necessary to use gas-governors and pressure gauges. At first the apparatus used in testing coal-gas was used, but proved too clumsy for the special use to which it was put. Ultimately a simple glass apparatus was devised, which is now described (Fig. 1).

A is a glass tap with long pointer and scale mounted on wooden block, *b*, *c*, and *m* are rubber connections, *d* is a piece of glass rod drawn out with a long tail, *e* is a piece of glass Sprengel tube blown with a bulb at one end and then ground down, *F* is a float weighted with mercury and having a platform of flat gas cemented on, *K* is a piece of wide glass tube, and *J* is a glass cylindrical jar. The point of entry of the gas is at *n*, and the point of exit at *X*. When in work, the pressure of the incoming gas depresses the water in the pressure tube to *z*, but the gas does not pass through this tube, but passes on into the chamber containing the valve made by *d* and *e*. The rate at which the gas passes through this valve depends upon the position of the float *F*, which is kept hovering about a position determined by the level *h* according to the exact dimension of the instrument. The level of water *g* is dependent on the amount of water placed in the jar *J*, and is easily adjusted before operations commence. The height *gh* is in consequence fixed once for all, the height *gi* shows the pressures of the incoming gas, the height *hi* shows the surplus pressure which is being got rid of by the valve *de*, and which is liable to variations due to irregular action in the other parts of the apparatus.

As the difference of pressure on the two sides of the tap is kept constant and the tap is fixed by trial, both pressure

\* Read before the University of Durham Philosophical Society, November 24th, 1911.



and resistance are constant and therefore current is constant also, unless the specific gravity of the gas should vary. Within certain limits the pressures and resistances before *n* and after *X* may vary, but the current of gas remains constant.

The records from twenty-two actual runs with this

of writing paper twisted two or three times round, and the remainder of the apparatus the ordinary body of a thermostat.

The rod *a* serves as the fine adjustment and renders unnecessary the restriction commonly placed at *g*. The rod and tubes fit one another fairly closely so that the

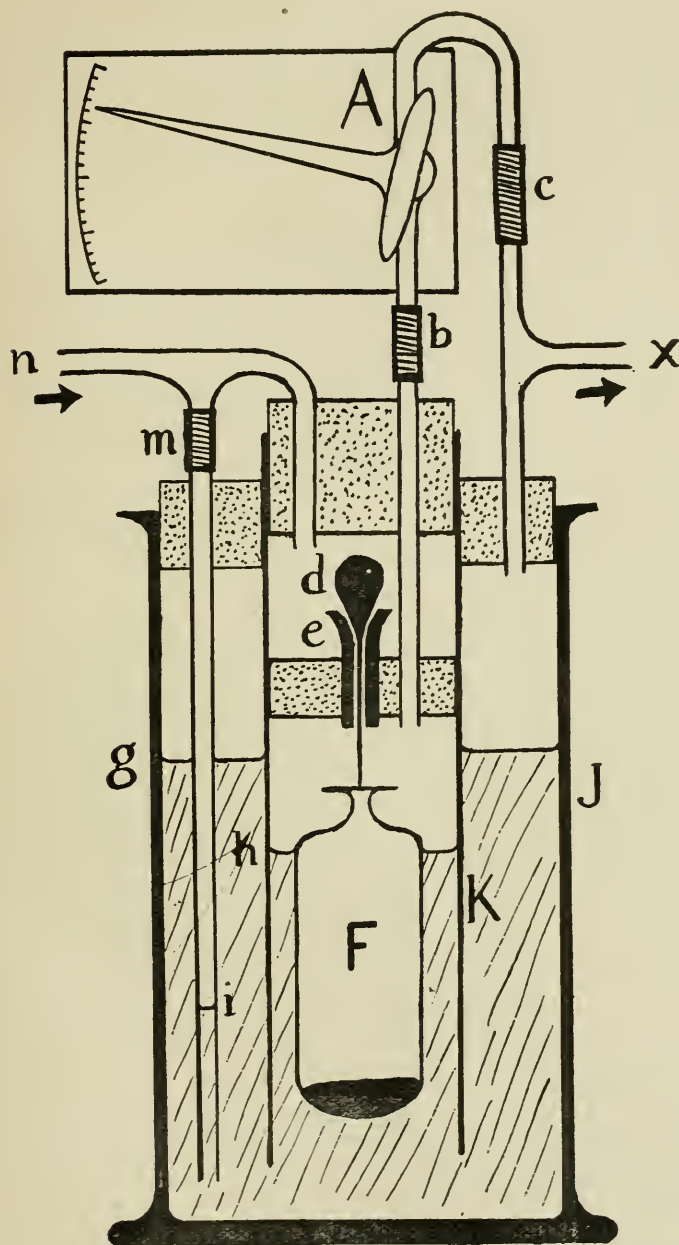


FIG. 1.

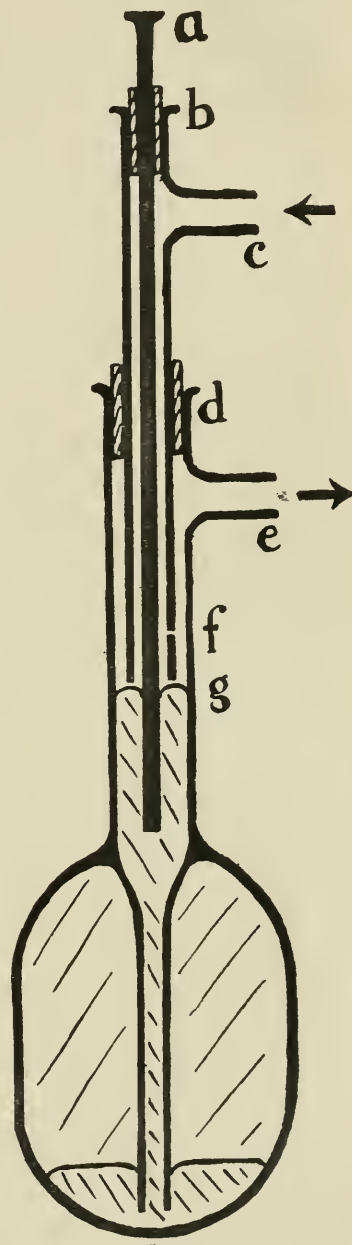


FIG. 2.

instrument show an average flow of  $10.05 \pm 0.22$  litres of gas per hour, when 10 litres was the flow required. This rate includes stopping and starting and long intervals of one or two hours without attention.

In diagram of the thermostat (Fig. 2), *a* is a thin glass rod, *c* is a T-piece with bye-pass at *f*, *b* and *d* thin strips

cross section of mercury at *g* is small. The close fit is rendered possible by the use of paper coils at *b* and *d* instead of corks. Experience shows that these paper coils are quite gas-tight. The T-piece *c* serves as coarse adjustment, gas-inlet, and bye-pass. The bulb contains mercury and toluene or other organic liquid with high coefficient

of expansion. The bulb may be made long and narrow if required. The thin glass rod *a* may be replaced by a knitting needle.

In use the T-piece *c* is approximately adjusted and then the rod *a* moved up and down for fine adjustment. Actual records of 215 observations gave an average temperature of  $45.04^{\circ}\text{C.} \pm 0.10$  for  $45^{\circ}\text{C.}$  intended.

(We are indebted to the Author for the woodcuts illustrating this Paper).

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

Ordinary Meeting, May 9th, 1912.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"Variation with Temperature of the Rate of a Chemical Change." By A. VERNON HARCOURT, F.R.S.

In an inquiry into the connection between the conditions of a chemical change and its amount, one of the conditions varied was that of the temperature of the solution in which the change took place (*Phil. Trans.*, 1895, clxxxvi., A, 817—895). A relation was found to exist between this condition and the rate of change, expressed by the equation  $a_T/a_{T_0} = (T/T_0)^a$ , where *a* is the rate of change, or the number of minutes in which a definite portion of chemical change is accomplished, *T*<sub>0</sub> the absolute temperature  $273^{\circ}$ , and *T* any other absolute temperature.

Not only do the numbers found from this equation agree very closely with the observed numbers, but the equation expresses a natural law which is nearly related to that upon which all calculations of gaseous volumes have long been based. For as a highly probable extrapolation shows that at  $-273^{\circ}\text{C.}$  the tension of gases falls to zero, and it is inferred that molecules cease to move, so it appears from these observations that this same figure represents the highest temperature at which chemical change does not take place, and atoms cease to move. At this temperature silicon and fluorine, potassium, and nitric acid, would lie down together; silver would not tarnish nor iron rust.

Several later measurements of the rate of change at different temperatures have been published and compared with numbers calculated from other formulæ. In an appendix to the present paper it is shown, by one of the authors of the previous paper, that the numbers thus calculated are in less close agreement with the actual measurements than numbers calculated from his formula given above, while also the formulæ have no physical interpretation. His colleague has, at the same time, made some observations on another case of chemical change, of which the following is a summary:—

When stannous chloride is added to the deep red liquid made by mixing solutions of ferric chloride, hydrogen chloride, and potassium sulphocyanide, the ferric salt is gradually reduced, and the red colour fades. The warmer the liquid is the more quickly does this happen. Observations of the rate of change were made by mixing these substances in a glass cylinder, by the side of which was placed a similar cylinder containing the same volume of a mixture of solutions of potassium sulphocyanide and hydrogen chloride with a smaller quantity of ferric chloride. This cylinder and its contents were kept as a standard, corked and in the dark when not in use, deep red but translucent. A second much paler standard was made up similarly, but with only two or three drops of the ferric chloride solution.

A few minutes after the admixture with stannous chloride the liquid in the reagent cylinder, which at first is nearly black and opaque, approached in appearance the dark standard. The observer, watch in hand, looked at the two at intervals of about two seconds, and noted the

time when they could no longer be distinguished. The temperature of the liquid was watched from the beginning, and kept as nearly as possible constant.

When the colour had nearly faded to that of the pale standard, a second comparison was made, and the time noted. The interval between the two observations was the time in which, at each chosen temperature, one and the same piece of chemical work had been done. Such a pair of observations was made at every three degrees from  $9$  to  $30$ , and of such sets of observations three were made under very nearly the same conditions. The times given below are the mean of the three sets, and those below them represent rates calculated from the equation  $a_T = 0.00845(T/T_0)^{23.5}$ , being their reciprocals, or the times in which the piece of chemical work would be done at those rates.

|              |             |              |              |              |              |              |              |              |
|--------------|-------------|--------------|--------------|--------------|--------------|--------------|--------------|--------------|
| Temps. ..    | $9^{\circ}$ | $12^{\circ}$ | $15^{\circ}$ | $18^{\circ}$ | $21^{\circ}$ | $24^{\circ}$ | $27^{\circ}$ | $30^{\circ}$ |
| Time (mins.) | 47.2        | 34.9         | 25.9         | 19.1         | 14.6         | 10.8         | 8.0          | 6.1          |
| Calculated.. | 47.2        | 34.9         | 25.9         | 19.3         | 14.4         | 10.8         | 8.1          | 6.1          |

When the proportion of hydrogen chloride is increased the rate also increases. A set of observations was made over the same series of temperatures in which the intervals were about one-third of those above. The observed and calculated times were in almost as good agreement.

An addition of hydrogen sulphate diminishes the rate; an addition of hydrogen nitrate leaves it nearly, if not quite, unaltered. The cause of the former may be that ferric sulphate is less easily reducible than ferric chloride. An increase of potassium sulphocyanide increases the rate, and so does an addition of sodium chloride.

The work that has been done is suggestive of much further work on the same lines, and the author hopes that it may now attract the interest, and pass into the hands, of some younger chemist, to whom he would gladly give any help which his experience of such work might enable him to give.

"Some Phenomena of Sunspots and of Terrestrial Magnetism at Kew Observatory." By C. CHREE, Sc.D., LL.D., F.R.S., Superintendent, Kew Observatory.

An investigation made some years ago by the author indicated the probability that a relation existed between the amplitude of the daily range of the magnetic elements and the sunspot area, not on the same day but several days previously. The object of the present research was to inquire into the reality of this connection. A selection was made of the five days of each month of the eleven years 1890 to 1900 which had the largest sunspot areas as given by the Greenwich annual lists. Mean values of the sunspot areas were derived for the 650 days thus selected (two months were omitted as having less than five days showing any sunspots), and for thirty other groups of days of the same number, corresponding to the fifteen days immediately preceding and the fifteen days immediately succeeding each of the 650 selected days. In this way one got thirty-one representative successive days, of which the central day had about twice as large a sunspot area as the average. The sunspot area rapidly and regularly declined on either side of the central day to an almost dead level, thus giving a very prominent "pulse" of sunspot area. The Kew daily horizontal force ranges were got out for the 650 representative days of large sunspot area, and the allied 19,500 days, and mean values obtained again for the thirty-one representative days. These mean values gave a marked pulse, corresponding to the sunspot area pulse, but with its crest about four days later. They gave also a minor or secondary pulse about fifteen days prior to the principal pulse. Several attempts were made to arrive at the cause of the secondary pulse. It was found to be largely a disturbance effect. In investigating its nature, it was found that there is a well-marked period of about 27.3 days in magnetic phenomena, in this sense, that if a certain day exhibits magnetic disturbance attaining the international standard "2," as interpreted at Kew, a day which follows either twenty-seven or twenty-eight days after has nearly double the chance of attaining standard



"2" that the ordinary day has. This twenty-seven to twenty-eight day period was not so clearly shown in the years of maximum sunspot frequency of the epoch considered as in the years of minimum frequency, and was most clearly shown in certain intermediate years characterised by the number than by the magnitude of magnetic disturbances.

The conclusion that a period of about 27·3 days exists in "magnetic storms" had been reached some years ago by Mr. Arthur Harvey and Mr. E. W. Maunder, independently, considering respectively data from Toronto and Greenwich, but their conclusions have not been universally accepted. The present investigation shows that the phenomenon is not confined to the large disturbances usually termed "magnetic storms," but is exhibited in the daily range of the average day.

"Ultimate Lines and the Quantities of the Elements producing those Lines in Spectra of the Oxyhydrogen Flame and Spark." By Sir WALTER NOEL HARTLEY, F.R.S., and HENRY WEBSTER MOSS, A.R.C.Sc.I., A.I.C.

In a recent paper by one of us (Hartley, *Proc. Roy. Soc.*, 1911, lxxxv., 271) on some mineral constituents of a dusty atmosphere as determined both by flame and spark spectra, a brief reference was made to the method employed for ascertaining the weights of matter necessary to give calcium and copper lines in the spark. This work has been extended to about twenty elements. The quantities of the elements which render the ultimate lines in the oxyhydrogen flame spectra had previously been carefully determined. With the alkali metals it is found to vary between 0·0008 mgrm. in the case of potassium, 0·01 mgrm. rubidium and caesium, and 0·1 mgrm. lithium. In the alkaline earth group, 0·01 mgrm. strontium, 0·1 mgrm. calcium, and barium 1·0 mgrm. Silver, 0·1 mgrm.; copper, 1·0 mgrm.; and gold, 50 mgrms. Gallium, iridium, and thallium, 0·01 mgrm.; manganese, 0·001 mgrm.; lead, 0·1; and tin, 100 mgrms. The gold spectrum shows the heads of very strong bands which correspond with lines in the spark spectrum. Tin shows no lines, but the edges of bands or flutings which are enfeebled until scarcely visible.

The method of determining ultimate lines in spark spectra and the quantities of matter volatilised in the spark when solid elements or metallic amalgams are used is fully described. The procedure was to expose a photographic plate (panchromatic) in a quartz spectrograph to a number of spark discharges both with and without self-inductance, and descending from twenty discharges to one, in order to eliminate all but the ultimate lines. The electrodes were weighed both before and after a number of sparks had been passed. The average weight of calcium, for example, volatilised from the negative electrode solely during sixty seconds, was 0·0002 grm., that is per second 0·00003 grm.; for each spark discharge the quantity is 0·00006 to 0·00004 mgrm.

Similar experiments were made with pure fused manganese, also with a solid amalgam containing 3·4 per cent of manganese. Many elements with only one spark discharge yield groups of lines; for example, manganese, twenty-seven lines are rendered by 0·00007 mgrm. of metal, and three lines by the amalgam from 0·000002 mgrm. of manganese. The most striking example is that of uranium. With five discharges = 0·001375 mgrm. all the lines in the spectrum from 4627·3 to about 2699 (Exner and Haschek) appear faintly, and they give almost a continuous spectrum. With one discharge = 0·000275 mgrm. a group of three lines appears faintly, all of equal intensity. Aluminium with one spark discharge = 0·000036 mgrm. renders the line 3587·0 quite distinctly; it is the ultimate line. It is interesting to observe that calcium line 3933·8 appears on the aluminium spectrum with five discharges. It undoubtedly came from dust in the air.

The object in obtaining these data is to apply them in the spectro-chemical analysis of minerals, alloys, and metals.

"Transformations of the Active Deposit of Thorium." By E. MARSDEN and C. G. DARWIN.

The present paper is concerned with a series of experiments undertaken with a view to discovering the genetic arrangement of the various products in the active deposit of thorium, and more particularly the transformations occurring in the product or products included in thorium C. These transformations are of particular interest and importance, for it is shown that there is in this case undoubted evidence that the atoms of a single kind of matter possess two distinct modes of disintegration. The results give strong reason for supposing that of the atoms of thorium C, 35 per cent emit  $\alpha$ -particles of range 4·8 cm., and become converted into atoms of thorium D, while the remaining 65 per cent emit  $\beta$ -particles, and disintegrate into atoms of a very short-lived  $\alpha$ -ray product thorium C<sub>2</sub>. Exhaustive attempts by chemical and physical methods and by recoil failed to separate the atoms giving the different radiations.

The experiments also show that although the  $\beta$ -rays of thorium C are extremely penetrating ( $\mu = 13·5 \text{ cm.}^{-1}$ Al), yet they are practically unaccompanied by  $\gamma$ -rays, while the relatively soft  $\beta$ -rays of thorium D are accompanied by a very intense penetrating  $\gamma$ -radiation containing over six times the amount of energy of the  $\beta$ -rays.

" $\beta$ -Particles Reflected by Sheets of Matter of Different Thicknesses." By W. WILSON, M.Sc.

1. The radiation reflected when the  $\beta$ -particles from uranium (*loc. cit.*) strike a screen can be split up into two parts, one with a very large coefficient of absorption, and the other with absorption coefficient of the same order as that of the primary beam.

2. The absorption coefficient of the more penetrating part of the reflected beam decreases with increasing thickness of the reflector.

3. The final absorption coefficients of the rays reflected from thick sheets of aluminium, copper, and lead are 33·7, 26·6, and 20·2  $\text{cm.}^{-1}$  respectively.

4. The coefficient of absorption of the easily absorbed part of the radiation reflected by aluminium is about 235  $\text{cm.}^{-1}$ . The absorption coefficients of the corresponding rays reflected from copper, lead, and air have not been determined with any degree of accuracy, but are of the same order of magnitude as that of the rays reflected by aluminium.

5. An expression has been obtained for the variation of the amount of reflected radiation with the thickness of the reflector, and has been shown to be in good agreement with the results obtained experimentally by Schmidt.

## CHEMICAL SOCIETY.

Ordinary Meeting, May 2nd, 1912.

Prof. E. J. MILLS, D.Sc., F.R.S., Vice-President, in the Chair.

CERTIFICATES were read for the first time in favour of Messrs. Cyril Douglas Birks, Cobnar Gardens, Woodseats, Sheffield; William Henry Bowater, School of Mines, Charters Towers, Queensland; Alfred Varlow Campbell, Rothamsted Experimental Station, Harpenden; Bamacharan Chatterji, M.A., Scottish Churches College, Calcutta; George Cruden Dieffenthaler, 7, Darceuil Lane, Belmont, Port of Spain, Trinidad; Leonard Harding, Fern Lea, Russell Street, Eccles; Harold Heron, 110, Fenchurch Street, E.C.; Thomas John Keenan, 751, East Nineteenth Street, Brooklyn, U.S.A.; Percival Edward Meadon, B.A., 6, Stanley Road, Oxford; Eric Keightley Rideal, B.A., 28, Victoria Street, S.W.; Percy Wharton Waters, Glenbervie, Melrose Avenue, Brooklands, Sale, Manchester.

A Ballot for the election of Fellows was held, and the following were subsequently declared duly elected:—Daniel Arkell, B.Sc.; Arthur Leslie Bartow; Arthur

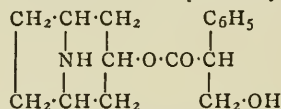
Anderson Bones; Ernest Gower Bryant; Charles Rugeley Bury, B.A.; Jatindranath Chakraborty, B.A.; Evelyn Ashley Cooper, B.Sc.; Raymond Edwin Crowther; William Dallas; Robert Percy Douglas; Frederick Charles Eastick, B.A.; Elliott Alfred Evans; John Burke Farlie, jun.; Edward Percy Frankland, B.A., Ph.D., M.Sc.; Walter Elmslie Hawkins, B.Sc.; James Grainger Hill; Oliver Richard Howells, B.Sc.; John Owen Hughes, B.Sc.; Edgar Dingle Jones; Richard Arnold Seymour-Jones, M.Sc.; Archibald Knox; Edwin Charles Lacey, B.Sc.; Leslie Herbert Lampitt, M.Sc.; Harold John de Quetteville Lenfestey; William Thornton Lucas, B.A.; Ambat Kesava Menon, B.A.; Robert John Milbourne; James O'Mara, B.A.; George Macauley Painter, B.Sc.; John Rennie; Henry Alfred Shute, B.Sc.; Bawa Kartar Singh, B.A.; Arthur Thompson; John Scott Thompson; George Walker; Arthur Wallace, B.A., B.Sc.; Frederick George Whittick; Charles Reginald Wilkins, B.Sc.

Of the following papers those marked \* were read:—

\*102. "Nor-hyoscyamine and Nor-atropine; Alkaloids occurring in various Solanaceous Plants." By FRANCIS HOWARD CARR and WILLIAM COLEBROOK REYNOLDS.

Nor-hyoscyamine—the secondary base corresponding with hyoscyamine—was described, and shown to occur in a number of different species of plants of the natural order Solanaceæ, namely, in *Scopolia japonica*, *Datura metel*, *Datura meteloides*, *Duboisia myoporoides*, and *Mandragora vernalis*, all of which also contain hyoscyamine.

The chemical constitution is expressed by the formula:—



which is supported by the evidence:—(1) That the alkaloid contains no NMe group; (2) that it forms a nitrosoamine, and therefore contains an :NH group; (3) that methyl iodide reacts with it, forming hyoscyamine; and (4) that it yields by hydrolysis tropic acid and nor-tropanol—a previously known base.

Nor-hyoscyamine is laevorotatory, and is racemised by the action of dilute alkali. The racemic base, nor-atropine, gives atropine on methylation with methyl iodide. It therefore bears the same relation to atropine as nor-hyoscyamine does to hyoscyamine.

The properties of these two new alkaloids and their salts were described. Evidence was given to prove that the supposed isomeride of hyoscyamine, called  $\psi$  hyoscyamine, described by Merck, is in reality nor-hyoscyamine.

The best method of distinguishing nor-hyoscyamine and nor-atropine from each other and from the other mydriatic alkaloids, is by the melting-points and crystalline form of various salts, particularly the oxalates, aurichlorides, and picrates.

Nor-hyoscyamine and nor-atropine produce contraction of the pupil of the eye of the cat, but the activity is about one-eighth that of the corresponding N-methyl derivative.

\*103. "Researches on the Constitution of Physostigmine." Part I. By ARTHUR HENRY SALWAY.

Physostigmine, when distilled with zinc dust, yields a mixture of 1- and 2-methylindoles. The author concludes that physostigmine contains a benzene nucleus attached to nitrogen, whilst it is not improbable that the atomic grouping,  $\text{C}_6\text{H}_4\text{C} \begin{smallmatrix} \diagup \text{N} \diagdown \end{smallmatrix} \text{C}$ , is also present in the alkaloid.

The hydrolytic product of physostigmine, namely, eseroline,  $\text{C}_{13}\text{H}_{18}\text{ON}_2$ , first prepared by Ehrenberg in 1893, has been found to be a monacidic tertiary base, containing one methyl group attached to nitrogen. Its hydrochloride, picrate, and methiodide were described.

The oxidation products of physostigmine and eseroline have also been investigated. The so-called "eserine blue"

has now been isolated in a pure condition. This base,  $\text{C}_{17}\text{H}_{23}\text{O}_2\text{N}_3$ , yields crystalline salts with two equivalents of an acid. It has an intensely blue colour, and in the presence of acids shows a brilliant carmine-red fluorescence.

When physostigmine or eseroline is allowed to absorb two atoms of oxygen in the presence of alkalis, rubreserine,  $\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_2$ , is formed. This substance, previously isolated by Eber (*Pharm. Zeit.*, 1888, xxxiii., 611), has been re-examined. It is a neutral substance, but yields salts both with acids and bases. Its aurichloride, hydrochloride, picrate, and silver salt were described.

\*104. "The Resolution of Benzoylalanine into its Optically Active Components." By WILLIAM JACKSON POPE and CHARLES STANLEY GIBSON.

The equilibrium method of Pope and Peachey can be conveniently applied in the resolution of externally compensated benzoylalanine into its optically active components. The rotation constants of d- and l-benzoylalanine have been determined in a number of solvents for mercury-green, mercury-yellow, and sodium light.

105. "The 'True' Ionisation and Hydration Constants of Ammonia and some Amines, with a Note on the Formulation of Nitrogen Compounds." By TOM SIDNEY MOORE.

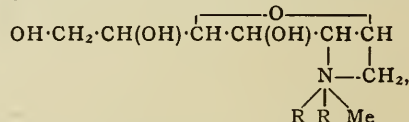
The author has applied the method of calculation previously described by him (*Trans.*, 1907, xci., 1373) to the results of the measurements of the partition-coefficients and "apparent" ionisation constants of ammonia, the methylamines, the ethylamines, and primary and secondary propylamines carried out by Winmill (*Proc. Chem. Soc.*, xxviii., 109). The results do not bring to light any simple relation between the constitution of an amine and the value of its ionisation constant and hydration constant, but show that there is a great contrast in ionising power between the quaternary hydroxides and the hydroxides of primary, secondary, and tertiary amines.

A modification of Werner's theory of ammonium compounds has been proposed to explain the observed relations.

106. "The Conversion of d-Glucosamine into d-Glucose." By JAMES COLQUHOUN IRVINE and ALEXANDER HYND.

The essential results of this investigation have already been published in a preliminary note (*Proc. Chem. Soc.*, 1912, xxviii., 54).

It has now been found that  $\alpha$ -aminomethylglucoside and its N-alkyl homologues, which are obtained as intermediate compounds in the conversion of glucosamine into glucose, are not to be regarded as simple glucosides. The reactions of the free bases are best explained by the general structure:—



where R = the methyl group or hydrogen. It was also shown that many of the reactions of glucosamine may be explained in terms of a formula of the above type.

The possibility of the conversion of glucosamine into glucose being accompanied by a Walden inversion was discussed, and reasons were given for the conclusion that a structural change of this nature does not take place. Glucosamine may thus be regarded as  $\alpha$ -amino-d-glucose.

107. "Chlorination of Iodophenols. Part I. The Chlorination of p-Iodophenol." By SIDNEY ALBERT BRAZIER and HAMILTON MCCOMBIE.

When an ice-cold solution of p-iodophenol in carbon tetrachloride is saturated with chlorine, an iodo-dichloride separates, which decomposes with evolution of hydrogen chloride, and the formation of 2-chloro-4-iodophenol. This compound, in turn, when chlorinated, yields an unstable iodo-dichloride, which, on decomposition, furnishes 2:6-dichloro-4-iodophenol. In a similar way, 2:3:6-tri-



chloro-4-iodophenol and 2:3:5:6-tetrachloro-4-iodophenol can be obtained.

In contradistinction to the free phenols, the acetyl and the benzoyl derivatives yield extremely stable iodo-dichlorides, which have been prepared and analysed. There is one exception to this, namely, the acetyl derivative of *p*-iodophenol, the iodo-dichloride of which decomposes after being kept for ten days.

When a solution of *p*-iodophenol in carbon tetrachloride kept at a temperature of 50–60° is saturated with chlorine, there are obtained 2:3:5:6-tetrachloro-4-iodophenol, pentachlorophenol, 2:3:4:4:5:6-hexachlorocyclohexadienone (Zincke and Schaum, *Ber.*, 1894, xxvii., 546), and chloroanil.

It was found that no iodo-dichloride could be prepared when the two ortho-positions relative to the iodine atom were occupied by chlorine atoms. This is in agreement with the observations of Willgerodt (*Ber.*, 1910, xliii., 2755; *Annalen*, 1911, cccclxxxv., 351).

Another interesting case of steric hindrance was encountered in attempting to prepare the benzoyl derivatives of phenols in which the two ortho-positions relative to the hydroxyl group were occupied with chlorine atoms. The ordinary Schotten-Baumann reaction failed in these cases, but the pyridine method yielded quite satisfactory results.

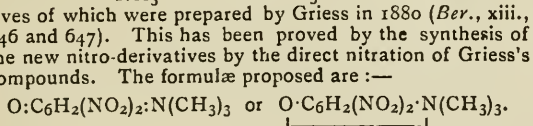
108. "The Monohalogen Derivatives of Acenaphthene." By HOLLAND CROMPTON and MAGGIE WALKER.

The preparation and some of the physical properties of chloro-, bromo-, and iodo-acenaphthene were described. The melting-points of mixtures of these compounds with each other, and also of their mixtures with acenaphthene, have been determined. Chloro- and bromo-acenaphthene form isomorphous mixtures, but there is no indication of the formation of such mixtures in any of the other cases.

109. "Quinone-ammonium Derivatives. Part I. The Methylation Products of Picramic and isopicramic Acids." By RAPHAEL MELDOLA and WILLIAM FRANCIS HOLLELY.

The product of extreme methylation of isopicramic acid by methyl sulphate in presence of alkali described in a preliminary note published in 1910 (*Proc. Chem. Soc.*, xxvi., 232) has been studied in detail, and its composition as a trimethyl derivative confirmed. The production of a similar compound from picramic acid has also been observed. Full consideration of the possible formulæ for these compounds has led to the conclusion that they are nitro-derivatives of the hypothetical quinone-ammonium

type,  $C_6H_4 \begin{smallmatrix} O \\ | \\ NH_3 \end{smallmatrix}$  or  $C_6H_4 \begin{smallmatrix} O \\ || \\ NH_3 \end{smallmatrix}$ , the trimethyl derivatives of which were prepared by Griess in 1880 (*Ber.*, xliii., 246 and 647). This has been proved by the synthesis of the new nitro-derivatives by the direct nitration of Griess's compounds. The formulæ proposed are:—



Alternative formulæ in which one of the nitro-groups assumes the "aci"-form have also been considered, and the question of internal linking is for the present left undecided. The compound from isopicramic acid forms a scarlet hydrate, which becomes ochreous on drying owing to conversion into the quinone-ammonium derivative. The authors have discussed in a preliminary way the connection between the colour and chemical constitution of these compounds, and have arrived at the conclusion that the red hydrate has the structure of a "quinole."

110. "Latent Heats of Vaporisation of Mixed Liquids. Part III. Mixtures of Associated with Non-associated Liquids. New Criteria for the Detection of Solvates in Mixtures of Liquids." By DANIEL TYRER.

In continuation of previous work, the latent heats of mixed liquids have been determined in the following cases:—(1) Benzene and ethyl alcohol; (2) chloroform and methyl alcohol; (3) chloroform and acetone; (4) carbon tetrachloride and ethyl alcohol.

In each case one of the constituents is an associated liquid. In addition, determinations have been made of the boiling-points of the mixtures and the compositions of the mixed saturated vapours. It was found that case (3) gives a maximum boiling-point, and the other three cases all give minimum boiling-points. At these maximum and minimum points the curves for the latent heats at constant pressure and constant composition intersect. By the aid of the additive law of mixtures, which was previously shown to be approximately true for latent heats, the apparent latent heats of the associated constituents in each mixture have been calculated. It was found that, as the concentration of the associated constituent diminishes, its apparent latent heat, instead of gradually diminishing as would be expected as a result of the progressive dissociation of the associated molecules, in all cases increases, at least over a portion of the range.

This was shown to be clear indication of the existence of solvates in these mixtures.

111. "Nickelo- and Palladio-dithio-oxalic Acids." By HUMPHREY OWEN JONES and CHARLES STANLEY ROBINSON.

The highly coloured and stable complex salts derived from the dibasic acids, nickelo- and palladio-dithio-oxalic acids, were described in a former paper (*Trans.*, 1912, ci., 62). These two acids have now been isolated and examined.

Nickelodithio-oxalic acid,  $Ni(COS)_4H_2 \cdot 4H_2O$ , separates from aqueous solutions in lustrous black prisms, often exceeding 1 cm. in length. Solutions of the acid have higher electrical conductivities than equivalent solutions of sulphuric acid. The acid decomposes in solution at 100° to give four grm.-molecules of hydrogen sulphide and one of nickel oxalate from one grm.-molecule of the acid, together with oxalic acid, carbon monoxide, and carbon dioxide in variable proportions, the sum of the oxalic acid and carbon monoxide being one grm.-molecule.

Palladiodithio-oxalic acid,  $Pd(COS)_4H_2 \cdot 3H_2O$ , separates from concentrated aqueous solutions in small dark brown plates. It is a strong acid, but is less stable than the corresponding nickelo-acid.

112. "Dithiomalonates." By HUMPHREY OWEN JONES and CHARLES STANLEY ROBINSON.

By the action of potassium hydrosulphide on amyl dithiomalonate in alcoholic solution, potassium dithiomalonate,  $CH_2(COS)_2K_2$ , is obtained. This salt reacts with metallic salts in a very similar manner to potassium dithio-oxalate, and with aniline hydrochloride yields malonanilide and hydrogen sulphide.

The colour of the complex nickelodithiomalonate is perceptible at a dilution of 1 part of nickel in 4,000,000 of water, whilst that of the corresponding dithio-oxalate is perceptible at dilutions of 1 in 40,000,000.

Several salts of the complex nickelodithiomalononic acid,  $Ni[CH_2(COS)_2]_2H_2$ , and palladiodithiomalononic acid,  $Pd[CH_2(COS)_2]_2H_2$ , were described.

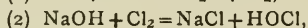
113. "The 'Crude Fat' of *Beta vulgaris*." By ALLEN NEVILLE.

The ethereal extract of the dry matter of the common mangel was examined and found to contain triglycerides, free fatty acids, and two neutral substances. The free and combined fatty acids consisted largely of palmitic, oleic, and erucic acids, whilst the two neutral substances were of phytosterol nature, and gave results on analysis corresponding with the empirical formulæ  $C_{31}H_{58}O_2$  and  $C_{29}H_{45}O_2$  respectively.

114. "An Experimental Investigation of the Bleaching Process. Part II. The Action of Neutral Salts on Bleaching Solutions." By SYDNEY HERBERT HIGGINS.

The author showed that chlorides of sodium and calcium stimulate the bleaching actions of chlorine-water and of hypochlorous acid, as well as that of hypochlorite solutions. In all cases the action is precisely the same; it is an immediate one, after which action the solutions behave as though the chlorides had not been added. These observa-

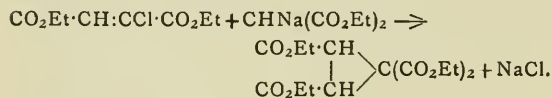
tions are opposed to the representation of the bleaching action of hypochlorites in the presence of chlorides as being due to the development of chlorine according to the equation  $\text{NaCl} + \text{NaOCl} + \text{H}_2\text{O} = 2\text{NaOH} + \text{Cl}_2$ , for this explanation does not account for the observations on the other bleaching solutions, and if it were true one would expect sodium chloride to cause a steady acceleration (and not a sudden action) as long as any sodium hypochlorite remained in solution. The reversible actions:—



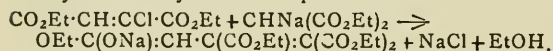
were found to explain all observations, including the behaviour of bleaching powder solution with neutral chlorides. The bleaching trials were performed on weak solutions of dye-stuffs, and on the colouring matters of cotton and linen cloth. In all cases practically the same results were obtained, showing that the same chemical actions took place during the oxidation of all the colouring matters used. The action of carbon dioxide on bleaching powder was discussed from equation (2) in support of the author's previous statement (*Trans.*, 1911, xcix., 858). Solutions of neutral salts were also found to decrease the stability of solutions of potassium permanganate in air and to increase their bleaching effect, so that for permanganate solutions, as for hypochlorites, it is evident that instability and bleaching effect are related.

115. "The Chemistry of the Aconitic Acids." (Preliminary Note). By NORMAN BLAND and JOCELYN FIELD THORPE.

A general method for the preparation of aconitic acid and of its alkyl derivatives has been found in the condensation of ethyl chlorofumarate and the sodium compound of ethyl malonate. Under ordinary conditions this condensation leads to the production of ethyl cyclopropanetetracarboxylate, thus (Ruhemann, *Trans.*, 1902, xlxxi., 1212):—

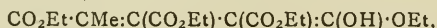


but in the presence of excess of sodium ethoxide ring-formation is prevented, and the yellow sodium compound of ethyl carbethoxyaconitate is produced:—



The sodium compound is not dissociated by water, and the aqueous solution yields the free ester when treated by carbon dioxide. From the fact that the ester is completely extracted by alkali from its solution in ether and gives a red coloration with ferric chloride, it follows that it is probably entirely enolic in structure. When hydrolysed by acids it is converted into aconitic acid.

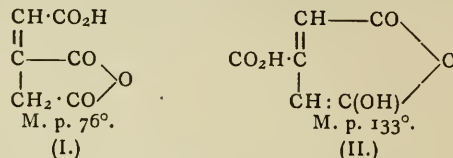
The action of methyl iodide on the sodium compound produces ethyl carbethoxy- $\gamma$ -methylaconitate (compare Ruhemann, *loc. cit.*, p. 1213), an ester which can be isolated in its structurally distinct ketonic and enolic forms. The *keto*-form,  $\text{CO}_2\text{Et} \cdot \text{CMe} : \text{C}(\text{CO}_2\text{Et}) \cdot \text{CH}(\text{CO}_2\text{Et})_2$ , boils at 215°/18 mm., gives no coloration with ferric chloride, and is not extracted from its solution in ether by aqueous alkali. The *enol*-form,



is an oil which is stable at the ordinary temperature, but passes slowly back to the ketonic modification on distillation. It gives a red coloration with ferric chloride, and is extracted from its ethereal solution by alkali.

It is hoped that by this method alkylated and dialkylated derivatives of aconitic acid can be prepared, and that a comparison of these substances with the corresponding derivatives of glutamic acid will supply important evidence respecting the influence exerted by the carboxyl group on the  $\beta$ -carbon atom of the three-carbon system.

Aconitic acid is a remarkable example of the different effect produced by a pure and an impure reagent on the course of a reaction. When treated with acetyl chloride containing phosphorus trichloride [Kahlbaum's acetyl chloride (II.)], it is quickly converted into the anhydro-acid (I.), melting at 76°, as found by Anschütz and Bertram (*Ber.*, 1904, xxxvii., 3967). If, however, pure acetyl chloride is used, dehydration takes place more slowly, and the product is the hydroxy-anhydro acid (II.):—



The hydroxy-anhydro-acid crystallises from ethyl acetate in needles which melt at 133°. It behaves on titration as a dibasic acid, and gives a deep reddish brown coloration with ferric chloride. It is probable that the anhydro-acid melting at 95° (Easterfield and Sell, *Trans.*, 1892, lxi., 1009) is a mixture of the two anhydrides mentioned above. The anhydro-acid melting at 76° is converted into the hydroxy-anhydro-acid melting at 133° by the action of acetyl chloride.

#### SOCIETY OF CHEMICAL INDUSTRY. (LONDON SECTION).

Ordinary Meeting, May 6th, 1912.

Mr. E. GRANT HOOPER in the Chair.

The following papers were read and discussed:—

"New Apparatus for the Coking Tests of Coal." By R. LESSING.

The author discusses the methods for the estimation of volatile matter in coal and their accuracy. He classes the sources of error of the crucible test in two groups:—

1. Factors tending to increase the "volatile" value.
  - (a) Burning of coke in the more or less oxidising atmosphere.
  - (b) "Spitting" of coal-dust due to explosive character of gasification of some coals or rush of currents produced by the flame.
2. Factors tending to decrease the "volatile" value.
  - (a) Insufficient coking of the coal.
  - (b) Secondary catalytic decomposition of volatile products on the walls of the crucible.
  - (c) Decomposition of volatile products by radiation in the waste spaces of the crucible.
  - (d) Deposition of carbon during coking by too rapid primary decomposition of volatile coal substance.

He states that practically the only point on which uniformity was so far desired and attempted was the quantitative determination of volatile matter, too little consideration being given to the properties of the coke obtained.

The author devised an apparatus which will show more markedly the difference in the coke produced from various coals, and which at the same time permits us to observe the process of carbonisation in individual cases.

Its principal object is to do away with the waste space above the coal in the ordinary test. Instead of the crucible he uses a cylindrical tube of about 10 mm. internal diameter made of quartz glass or platinum. One grm. of powdered coal is placed into this tube and a quartz glass piston introduced which rests upon the coal, and the weight of which can be altered. The tube is placed into an outer tube of special design, which is electrically heated. The author observed very marked differences in the resultant coke when treating various coals in his apparatus. Photographs of cokes obtained from twenty different coals are



shown, of which the analyses are given. Another diagram compares the cokes obtained by the author's method with those obtained in the platinum crucible. A special feature of the apparatus is the possibility of identification, as every coal will invariably assume the same shape and structure of coke when treated in the apparatus. The quantitative results obtained in the author's apparatus and those according to the "American" method are compared.

The author claims usefulness of the apparatus for the study of carbonisation and for comparison and identification of coals.

*New Method for the Determination of Ferrocyanides.* By H. E. WILLIAMS.

The methods in general use for the estimation of ferrocyanides can be classed under two heads:—

1. Titration of the ferrocyanide with a solution of a metallic salt.
2. Decomposition of the ferrocyanide by suitable means into hydrocyanic acid.

In the former class extreme care and long experience is required, and it is necessary that the titration be performed under conditions exactly similar to that of the standard, and any variation will generally lead to discordant results.

In the latter class the chief difficulty is the complete decomposition of the ferrocyanide into hydrocyanic acid by distillation with dilute acids—this difficulty has been overcome in the method worked out by Field—whereby the ferrocyanide is converted first into mercuric cyanide by boiling with mercuric chloride, which on subsequent distillation with dilute acids yields the whole of its cyanogen as hydrocyanic acid, but, as has been shown by Skerrow (*Journ. Soc. Chem. Ind.*, March 31, 1910), and confirmed by the author, small losses occur in the preliminary boiling operations.

In the following process the losses above mentioned are avoided, and the process is both simple and accurate:—

Take 0.5 grain of ferrocyanide in 100 cc. of water and transfer to 250—300 cc. distilling flask, add 0.05—0.1 grain of cuprous chloride dissolved in a few drops of hydrochloric acid, and finally add 25—30 cc.  $\frac{4}{N}$  sulphuric acid and distil through a condenser into caustic alkali solution; the cyanide solution so obtained is titrated with silver nitrate in the usual manner.

By this means the whole of the ferrocyanide is decomposed, and the hydrocyanic acid obtained as an alkaline cyanide.

Any ferrocyanide may be estimated by this method, whether soluble or insoluble, without any preliminary operation. If, however, the insoluble ferrocyanide is taken in the dry state it must first be ground to a fine powder before adding to the distilling flask.

*"Drying Oven."* By J. H. COSTE.

The oven is heated by the vapour of water, toluene, or other liquid of suitable boiling-point. Loss of vapour is prevented by a small but efficient condenser. Substances to be dried are placed in a long muffle-shaped chamber, through which passes a current of air (or other gas) which has been pre-heated by the vapour of the boiling liquid. When air is used, a chimney in the door provides a sufficient natural draught.

The cubical capacity of the oven is very small, relative to the area of heated surface and the area of the door; the only part not exposed to the vapour is about  $\frac{1}{30}$  of the heated surface. A temperature within  $1^{\circ}$  C. of the heating vapour is obtained. Six watch-glasses or shallow weighing bottles can be heated together in the oven.

*"Indiarubber as a Protective Colloid. The Formation of Colloidal Metallic Sulphides in Rubber Solutions."* By E. W. LEWIS and H. WAUMSLEY.

When a strip of lead is immersed in a solution of rubber in benzole containing even traces of carbon disulphide, lead passes slowly into the solution, the latter acquiring a deep brown colour. In the entire absence of rubber no such change occurs, and with very low rubber concentra-

tions (e.g., 0.5 per cent.) the change is extremely slow. In 1 per cent solutions of rubber, however, a distinct coloration is evident in the course of a few days, even when the carbon disulphide concentration is as low as 1 per cent. The change is hastened by the addition of traces of alcohol (e.g., 0.1 to 0.4 per cent), and the speed is greater with high concentrations of carbon disulphide than with low. But the rubber concentration appears to be the most important factor in determining the rate of change. The darkening of the solution is probably due to the formation of a colloidal solution of lead sulphide under the "protective" influence of the rubber. The sulphide solution can be transformed into one of chloride by agitation with a drop of concentrated hydrochloric acid, or by means of sulphur chloride, and reconverted into sulphide by the action of ammonium sulphide solution. The sulphide is converted into iodide by the addition to the solution of a benzole solution of iodine, and some of the iodide remains in colloidal solution.

Copper behaves in a similar manner, and mercury apparently in a much less degree.

A similar result is also obtained in the case of lead when an acetone solution of celluloid containing carbon disulphide is employed in place of the rubber solution.

## NOTICES OF BOOKS.

*Historical Papers on Modern Explosives.* By GEORGE W. MACDONALD, M.Sc. (Melb.). London and New York: Whittaker and Co. 1912.

THE papers on modern explosives of which this book is composed originally appeared in the form of a series of articles in *Arms and Explosives*. They date back to Howard's discovery of fulminate in 1800, and give short accounts of the manufacture and investigation of modern explosives, more especially gun-cotton, both in this country and abroad. The author has made a careful summary of all the important work which has been published, and in most cases has followed the text of the original papers very closely, although a good deal of compression has sometimes been necessary. The book, to which Sir Andrew Noble has contributed a preface, will be found a useful compilation by all who are interested in the chemistry of explosives.

*Chemical Works. Their Design, Erection, and Equipment.* By S. S. DYSON and S. S. CLARKSON. London: Scott, Greenwood, and Son. 1912.

THE working drawings of the plant of chemical works constitute a valuable feature of this book, in which the authors have endeavoured to condense the results of their lengthy experience of the designing of such works. The chemical engineer will find that the book is of a thoroughly practical type, and is well up-to-date in every respect, giving a summary in which practical points are specially emphasised and which can be used satisfactorily in conjunction with theoretical treatises. The plants used in acid and alkali works are treated in successive chapters, and a long section is devoted to the general plant required in the equipment of a chemical works. In some respects the treatment of the subject shows a lack of a due sense of proportionality. For example, a considerable amount of space is devoted to the discussion of fire station appliances and "welfare work and profit sharing," and this entails some curtailing in other directions; thus the chapter on materials used in construction neglects stone, brick, wood, &c., and deals only with the metals and asbestos. Interesting and important as the subjects of accident treatment, fire extinction, and social work among the employees are, they are not chemical engineering, and should not be allowed to take up more than a very limited amount of space in a book of this size, which endeavours to cover so wide a subject.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. cliv., No. 14, April 1, 1912.

**Solution of Copper in Water.**—J. Pionchon.—When an electric cell is made by immersing two plates of the same metal in an electrolytic liquid, and one of the electrodes is struck a few sharp blows, the chemical relation of the metal and liquid is momentarily disturbed, and a current passes from the electrode which has been struck towards the other. This may be explained by supposing that the metal undergoes ionisation, and when copper and water are used it is found that traces of copper undergo solution in the water, although they cannot be detected by chemical methods.

**Dimethyl Ether of 1.5-Pentene-diol and its Hydrogenation.**—M. Lespieau.—The dimethyl ether of 1.5-pentene-diol can be prepared from the methyl ether of 1.4-butanediol by converting it into the mixed magnesium derivative and attacking the latter with chloromethyl ether. The substance has all the characteristics of a disubstituted acetylenic compound. When it is hydrogenated in presence of platinum black, in certain conditions the hydrogen may attack the ether oxide function yielding a saturated hydrocarbon. Methyl alcohol is produced at the same time.

*Berichte der Deutschen Chemischen Gesellschaft,*  
Vol. xlv., No. 5, 1912.

**New Silicon Carbides.**—Artur Bygdén.—The author has obtained tetra-alkyl silicenes, e.g.,  $(C_2H_5)_3Si(n-C_3H_7)$ , by the action of alkyl silicon chlorides on ethyl magnesium bromide, and hexamethyl-silicoethane,  $(CH_3)_3Si.Si(CH_3)_3$ , by treating silicon hexachloride with methyl magnesium bromide. Trialkyl-phenyl-silicenes can be prepared from phenyl silicon chlorides and alkyl magnesium bromides.

*Atti della Reale Accademia dei Lincei.*  
Vol. xxi., No. 4, 1912.

**Photosynthesis of an Alkaloid from Acetophenone and Ammonia.**—E. Paterno and C. Maselli.—The action of light on a solution of acetophenone in alcoholic ammonia yields a new alkaloid of formula  $C_{18}H_{18}N_2$ . It is a monacid base, and the authors have prepared some of its salts, e.g., the nitrate and the chloride, as well as a silver salt and a mononitroso derivative.

**Chemical Composition of the Embryo of Rice.**—Luigi Bernardini.—The embryo of rice contains a large amount of phosphorus, and in the ash of the embryo there is a considerable proportion of silica. The most important metals present in the ash are potassium and magnesium.

T. Barnes on "Icebergs and their Location in Navigation"; and on June 7th, by Sir William Macewen, on "Lord Lister." An extra Friday Evening Discourse will be given on June 14th by Mr. A. Henry Savage Landor on "Unknown Parts of South America" (Recent Journey, with Illustrations).

**International Rubber Congress and Exhibition.**—An International Rubber Congress and Exhibition will be held at Batavia in April, 1914. The Congress and Exhibition will be organised by the Netherlands Indies Agriculture Syndicate, which also brought about the very successful Fibre Congress and Exhibition at Sourabaya in 1911. Both Congress and Exhibition have the support of the Government of the Netherlands East Indies and many influential persons, commercial bodies, and estates. His Excellency the Governor-General of the Netherlands East Indies has kindly consented to become Honorary President of the Congress and the Exhibition, and has declared himself prepared to personally open the former. The consular representatives established in the Netherlands Indies have also been invited to become members of the Honorary Committee. A complete detailed programme of the Congress and the Exhibition will shortly be published and distributed on a large scale in all countries of the world. At this moment we can, however, state that both the Congress and the Exhibition will deal with all matters concerning rubber-production (wild and plantation-rubber) and the preparation of the crude product, in the broadest sense of the word, whilst other branches of the culture and industry, such as the production and preparation of balata, jelotong, and gutta-percha will also be given attention. It is hardly necessary to state that the rubber-culture and industry—which develop so rapidly—will be dealt with as regards their condition at the time of Congress, and that everything will be brought as much up to date as possible.

**Free Places at the Imperial College of Science and Technology, 1912.**—The London County Council will be prepared to award in July next a certain number of free places at the Imperial College of Science and Technology, South Kensington, S.W. These places will be filled as from October, 1912. The instruction will be of an advanced nature, and therefore only advanced students who are qualified to enter on the fourth year of the course should apply. There is no restriction as to income, but intending candidates must be ordinarily resident within the area of the administrative County of London, and must be students who have attended regularly appropriate courses of instruction for at least two sessions. The free studentships do not entitle the holders to any maintenance grants, but cover all ordinary tuition fees. No examination will be adopted for the final selection of the students. The free studentships will be awarded on consideration of the past records of the candidates, the recommendations of their teachers, the course of study they intend to follow, and generally upon their fitness for advanced study in science applied to industry. It is possible that in special cases the free places may be extended to two or more years. Application forms may be obtained from the Education Officer, L.C.C. Education Offices, Victoria Embankment, London, W.C., and must be returned not later than Saturday, May 25th, 1912.

## MISCELLANEOUS.

**Royal Institution.**—On Tuesday next, May 28th, at 3 o'clock, Prof. W. M. Flinders Petrie gives the first of two lectures at the Royal Institution on "The Formation of the Alphabet"; on Thursday, May 30th, Prof. C. G. Barkla begins a course of two lectures on "X-Rays and Matter"; and on Saturday, June 1st, Mr. Willis L. Moore, Chief of the United States Weather Bureau, will deliver the first of two lectures on "The Development and Utilities of Meteorological Science." The Friday Evening Discourse on May 31st will be delivered by Prof. Howard

## MEETINGS FOR THE WEEK.

TUESDAY, 28th.—Royal Institution, 3. "The Formation of the Alphabet," by Prof. W. M. Flinders Petrie, F.R.S.  
THURSDAY, 30th.—Royal Institution, 3. "X-rays and Matter," by Prof. C. G. Barkla, F.R.S.  
FRIDAY, 31st.—Royal Institution, 9. "Icebergs and their Location in Navigation," by Prof. Howard T. Barnes, F.R.S.  
— Physical, 5. "Calibration of Wave-meters for Radiotelegraphy," by G. W. O. Howe. "Use of Heavieside's Resistance Operators in Air-core Transformer Theory," by W. H. Eccles. "Movements of Semi-fluid Liquids on a Water Surface," by C. R. Darling.  
SATURDAY, June 1st.—Royal Institution, 3. "The Development of Meteorological Science," by Willis L. Moore.



# THE CHEMICAL NEWS.

VOL. CV., No. 2740.

## DECOMPOSITION OF WATER AT ORDINARY TEMPERATURES BY MAGNESIUM.

By ARTHUR W. KNAPP, B.Sc., F.I.C.

WHEN magnesium is mixed with water no reaction is observed at ordinary temperatures, although the formation of magnesium hydroxide and the liberation of hydrogen is an exothermic reaction. This is commonly explained by saying that the film of hydroxide first formed covers the metal and retards further action. However, if magnesium powder be added to ten times its weight of water, and then to this mixture such an amount of palladium chloride as contains about one hundredth part of the weight of magnesium used, a brisk evolution of hydrogen occurs. The magnesium reduces the palladium chloride and metallic palladium is formed, which acts as a catalytic agent. The small amount of magnesium chloride formed possibly also accelerates the reaction at first by dissolving the hydroxide. The temperature rapidly rises until the water boils and considerable white hydroxide is formed. The palladium, which has accelerated the decomposition of the water now accelerates its formation, for it is warm, and some of it rising on the bubble-films, which separate the hydrogen from the air, causes the hydrogen to ignite spontaneously.

## A NEW METHOD FOR THE DETERMINATION OF VANADIUM.

(AN EXPLANATION).

By J. R. CAIN and D. J. DEMOREST.

THE discrepancy in results obtained by us when using manganese dioxide, as mentioned in the paper on "A New Method for the Determination of Vanadium" (see p. 244), led us to seek the cause. We exchanged samples of manganese dioxide, and each found that the other's reagent behaved as stated in our respective papers. However, it was noted by Mr. Cain that Mr. Demorest's dioxide, which oxidised differentially, was much coarser than the manganese dioxide which the former had used, and which oxidised both the lower oxides of vanadium and iron. Upon grinding the coarse manganese dioxide very fine he found that it oxidised both iron and vanadium oxides as his own preparation had done. On the other hand, Mr. Demorest succeeded in separating a coarse portion from the manganese dioxide used by Mr. Cain which oxidised differentially.

Thus, the discrepancy is evidently due to a difference, in the two cases, of the velocities of the reactions:—

- (1)  $V_2O_4 + MnO_2 = MnO + V_2O_5$
- (2)  $FeO + MnO_2 = Fe_2O_3 + MnO$

Mr. Demorest's reagent had a degree of fineness such that in the brief period of treatment the velocity of reaction (1) was inappreciable and reaction (2) was completed; whereas with material of the fineness used by Mr. Cain both reactions went to completion. The securing of such different results merely by changing the size of the grain of the reacting solid seems a matter worthy of further investigation.—*Journal of Industrial and Engineering Chemistry*, iv., No. 4.

## TWO NEW AND VERY DELICATE TESTS BY USE OF THE REAGENT, "TETRAMETHYL BASE."

By ROBERT J. CARNEY.

AN acetic acid solution of the organic base, tetramethyldiaminodiphenylmethane,  $(CH_3)_4N_2(C_6H_4)_2CH_2$ , was used by Trillat in 1903 for the detection of traces of lead and manganese (*Comptes Rendus*, cxxxvi., 1205—1207; also *Journ. Chem. Soc. Abstr.*, 1903, p. 512). His method is to convert the metals into the form of dry sulphates, then warm and treat with a few drops of a solution of sodium hypochlorite, remove the chlorine by washing, and add the reagent and warm. A beautiful blue colour develops, which disappears on cooling and reappears on warming. With manganese it is not necessary to add the hypochlorite, but merely to add sodium hydroxide and ignite before adding the reagent. Trillat found that this gave a very delicate test for both lead and manganese.

This base has also been used as a reagent for the detection of ozone in mixtures containing hydrogen peroxide and the oxides of nitrogen. For this purpose the base is dissolved in alcohol, and strips of paper are moistened with the alcoholic solution and held in the gas. Ozone gives a violet colour, nitrogen dioxide a straw-yellow, and hydrogen peroxide no colour whatever. Arnold and Mentzel were the first to use the reagent for this purpose (*Ber.*, xxxv., 1324). They named the reagent "tetra base," but finding later that *p*-phenylenediamine had long been sold under this name, they changed the name to "tetramethyl base." Fischer and Marx (*Ber.*, xxxix., 2555), Fischer and Braehmer (*Ber.*, xxxix., 940—68), and Kaiser and McMaster (*Am. Chem. Journ.*, xxxix., 96), have also used this reagent in their work as a test for ozone.

A modification of Trillat's method has been used for some time in the University of Michigan Laboratory as a test for manganese, confirming the results obtained by inorganic tests. The base is prepared as follows:—Warm on the water-bath for one hour a mixture of 30 grms. of dimethylaniline, 10 grms. of formaldehyde, 200 cc. of water, and 10 cc. sulphuric acid. After cooling, make alkaline with an excess of sodium hydroxide, drive off the unchanged dimethylaniline with steam. Filter after cooling, wash the brownish product with water, then recrystallise once from alcohol. This gives a pure yellowish white product.

There are objections to the use of an acetic acid solution of the base, as recommended by Trillat. The acetic acid solution should be heated when used, but when heated the base immediately precipitates and will not dissolve until the solution is cooled. A colourless acetic acid solution of the base is hard to obtain. It is unstable and soon darkens, even though kept away from the light. The use of citric acid as the solvent has been found to be much more satisfactory. The reagent is made up by dissolving 2.5 grms. of the organic compound in a solution of 10 grms. of citric acid in 10 cc. of water. This solution is then diluted to 500 cc. It is perfectly colourless, will not give a precipitate upon heating even to boiling, and is stable, no precautions with regard to keeping out light being necessary.

With any compound of lead or manganese in which the metal has a valence of more than two, a cold solution of the reagent will give a deep reddish purple colour, due to an oxidation product of the reagent. Cobaltic and nickelic hydroxides also cause the formation of the colour, although the reaction takes place perhaps somewhat more slowly and the colour is not as deep usually as with manganese or lead. This test finds application in any of the ordinary systems of qualitative analysis. If the metals of the ammonium hydroxide group are separated from each other by the use of sodium peroxide or sodium hydroxide and hydrogen peroxide, the manganese which precipitates in this group will remain with the ferric hydroxide. If no cobalt or nickel is present, the ferric hydroxide precipitate

may be tested for manganese by washing it and pouring a small quantity of the reagent over it. The filtrate will have a deep reddish purple colour, if manganese is present. The original ammonium hydroxide precipitate may be tested for manganese by washing it thoroughly and allowing it to stand with free access of air for several minutes, then adding the reagent to a portion of the precipitate. Cobalt and nickel do not interfere. In the ammonium sulphide group, the manganese sulphide may be dissolved in cold dilute hydrochloric acid, the hydrogen sulphide boiled out, and manganese separated from zinc by the use of sodium hydroxide and bromine water. The precipitate of manganese dioxide should be thoroughly washed, and if cobalt and nickel are absent, the solution of the organic reagent may be poured over it. If cobalt or nickel is present the precipitate should be dissolved in hydrochloric acid with the addition of peroxide, if desired, and the manganese separated by the action of ammonium hydroxide and hydrogen peroxide. The resulting precipitate is washed and tested with the reagent. Another way of carrying out the test is to boil out the hydrogen sulphide from the hydrochloric acid solution of manganese sulphide, then add sodium hydroxide in excess, filter, wash thoroughly, let stand a few moments, and add the reagent. A rapid test for manganese, which may be used upon a solution containing all of the ordinary metals, consists in boiling the acidified solution to remove chlorine or other halogen, then adding sodium hydroxide in excess, filtering the precipitated hydroxides, washing, allowing to stand about ten minutes, and then adding the reagent. Lead, cobalt, nickel, and other elements give no colorations.

*Use of Reagent as a Test for Gold.*—No mention has ever been made of the action of this reagent upon salts of gold. With very dilute solutions of gold chloride, the reagent gives a very beautiful purple colour, due to the oxidising action of the gold salt; this soon changes to blue, and then becomes colourless. The blue colour reappears upon warming. With more concentrated solutions the colour is purple by transmitted light, and bluish to green by reflected light. It was found by working with very dilute solutions that this reagent affords a very delicate test for gold, not interfered with by platinum, palladium, or other elements. The colour is very much more distinct than "purple of Cassius." Free mineral acid interferes with the reaction. Solutions should be neutralised and made slightly acid with acetic or citric acid. To determine the delicacy of the test a gold solution was made up by dissolving 20 mgrms. of metallic gold in nitrohydrochloric acid. This was evaporated to remove chlorine, neutralised with sodium carbonate, and made slightly acid with acetic acid. The solution was then diluted to 1 litre. Portions of this solution were diluted to 50 cc. and tested with the reagent. The following table gives the results:—

| Au solution (cc.). | Gold (grm.). | Result.                     |
|--------------------|--------------|-----------------------------|
| 25                 | 0.0005       | Very fine purple colour.    |
| 5                  | 0.0001       | Good blue colour.           |
| 1                  | 0.00002      | Plainly visible light blue. |
| 0.5                | 0.00001      | Barely visible light blue.  |

The delicacy of the test in a solution containing nothing but gold is 0.01 mgrm. per 50 cc.

*Use as a Test for Ammonia.*—The test for ammonia makes use of the fact that hydrogen peroxide has no action upon a solution of a manganous salt unless an alkali is present. In the presence of even a trace of alkali the peroxide instantly oxidises the manganese to a brown higher oxide. The test is carried out by heating the solution supposed to contain the ammonium salt with sodium hydroxide in an Erlenmeyer flask fitted with a rubber stopper, through which passes a short glass tube, bent at right angles. A piece of filter-paper is moistened with a solution made up by dissolving 2 grms. of manganous sulphate in 200 cc. of water, and adding 5 cc. of the ordinary laboratory hydrogen peroxide solution. This filter-paper is held directly in front of the tube through which the

steam and ammonia are passing. If ammonia is present in any quantity a brown stain will appear upon the paper. This stain may be moistened with a drop of the organic reagent, and a deep purple colour will appear. The excess of hydrogen peroxide present has no effect upon the test. With exceedingly small quantities of ammonia no brown stain will be formed, but a purple stain will readily be obtained upon adding the reagent. Steam itself has no action if manganous sulphate is used. If manganous acetate is used, very slight purple stains may form, even when no ammonia is present. To test the delicacy of this test a solution of ammonium chloride was made up containing 63 mgrms. of ammonium chloride per litre, which would be equivalent to 20 mgrms. of ammonia per litre. The following table gives the results obtained:—

| NH <sub>4</sub> Cl solution (cc.). | NH <sub>3</sub> (grms.). | Result.                                                  |
|------------------------------------|--------------------------|----------------------------------------------------------|
| 25                                 | 0.0005                   | Very distinct brown colour. Very brilliant purple stain. |
| 5                                  | 0.0001                   | Faint brown colour. Very brilliant purple stain.         |
| 2.5                                | 0.00005                  | Faintly visible brown colour. Good purple stain.         |
| 1                                  | 0.00002                  | No visible brown stain. Distinct purple spot.            |
| 0.5                                | 0.00001                  | Slight bluish spot.                                      |
| Steam alone                        | —                        | No coloration.                                           |

It is possible, then, by this method to easily detect 0.02 mgrm. of NH<sub>3</sub>, and by carrying out carefully to be able to detect 0.01 mgrm.—*Journal of the American Chemical Society*, xxxiv., No. 1.

## THE PURIFICATION AND SOFTENING OF WATER BY PERMUTITE.

By W. A. HAMOR.

THE advantages to be gained by the use of soft water in steam raising, and for many manufacturing operations, are now generally recognised. It is also conceded that the presence of iron in water for dyeing, printing, bleaching works, and paper factories, is very undesirable. In brewing, too, water containing much iron is objectionable. Therefore the application of the product "Permutite," an artificial zeolite,  $3\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot (\text{K}_2\text{O} \cdot \text{Na}_2\text{O} \cdot \text{CaO}) \cdot 6\text{H}_2\text{O}$ , for the purpose of removing certain constituents from water and softening it, is of great interest to the chemist and engineer.

The Permutit-Filter Co., of Berlin, was organised in 1909 for the purpose of exploiting the above mentioned artificial zeolite under the trade name "Permutite" (see Appellius, *Chem. Rev. Fett-Harz. Ind.*, 1909, p. 300). This company devised also a process for softening water, and for relieving it of iron and manganese (English Patent 26,074, Nov. 9, 1910). A number of other foreign companies are now being organised for developing these methods of water treatment. The "Permutite" process has been operated on a commercial scale at Glogau for the removal of manganese from water.

R. Gans (*Mitt. aus. d. Koenigl. Profungsanst. f. Wasserversorgung u. Abwasserbeseitigung zu Berlin*, 1907, p. 8; *Woch. f. Brau.*, xxiv., 270) found that the aluminate-silicates exchanged their bases not only for alkalis and alkaline earths, but also for iron, manganese, lead, silver, and presumably for all metals. He pointed out that a filter of such material could be regenerated after use by washing with alkali salts, by which the metals separated from the water were re-dissolved. According to Gans, by fusing aluminium silicates with sodium carbonate and sufficient quartz to decompose all the carbonate aluminate-silicates containing 12 to 15 per cent Na<sub>2</sub>O are obtained which are excellent filtering media. He stated



that the soda content was of the greatest importance, since it was found to replace the bases present in the water. In one experiment conducted by Gans, well-water which rapidly became turbid in the air, owing to the separation of iron, was filtered through a 10 cm. layer of calcium aluminate, the water level falling 10 cm. per hour. The whole of the iron was removed from the water by the filter, from which it was afterwards dissolved by washing with sodium chloride solution.

Gans also made experiments on the softening of water for boiler-feed purposes. A hard water was treated with sodium aluminate-silicate, which was found to remove the lime and magnesia quantitatively, leaving only the alkali carbonates, sulphates, and chlorides, together with the small proportion of silicates contained in the original water. He found that if only three-fourths of the sodium of the sodium aluminium silicate was replaceable, 4.5 lbs. of the material would remove from 30 cubic feet of water possessing a hardness of 20° (German), all salts capable of forming boiler incrustation. Gans reported (*Chem. Ztg.*, xxxi., 355) that manganese could be separated from water by filtration through a layer of granular aluminium silicate, prepared by fusing clay with an alkali carbonate, and adding to the fused mass sufficient quartz to combine with almost the whole of the alkali. After extracting the mass with water, the silicate was obtained in a granular or flaky form. Regeneration of foul filtering layers was found to be accomplished by washing with calcium chloride or calcium-sodium chloride solution. Gans also reported that hydrated silicates, both natural and artificial, were capable of withdrawing the bases from alkaline and neutral salt solutions, and that potash and soda might be eliminated from sugar juice by means of aluminium silicate (*Z. Ver. Deut. Zuckerind.*, 1907, p. 206). In German Patent 174,097, of January 12, 1905, issued to Gans, it is pointed out that artificial zeolites or alkaline-earth aluminate-silicates for the purification of molasses need to be free from uncombined lime (see also French Patent 374,525, February 11, 1907, of the J. D. Riedel A.-G.; and United States Patent 943,535, December 4, 1909, of R. Gans for the manufacture of hydrated aluminium silicates).

In a patent issued to Gans in 1907 (English Patent 8232, April 9, 1907) the claim is made for the manufacture of hydrated aluminosilicates, or artificial zeolites. About this time Gans gave further evidence of the usefulness of aluminium silicates for improving water supplies (*J. Gasbeleucht.*, l., 1026); he pointed out that iron and manganese were removed completely by passing the water through a filter composed of calcium-aluminium silicate; that a hard water could be softened by filtration through sodium-aluminium silicate, the latter material also serving to remove any iron, manganese, and ammonia which might be present in the water; and recommended that in supplies where the hardness was due principally to calcium sulphate, the water be passed successively through layers consisting of strontium-aluminium silicate and calcium-aluminium silicate.

In 1908, Lührig and Becker (*Chem. Ztg.*, xxxii., 514, 531) conducted experiments on the efficiency of the "Gans method" for removing manganese sulphate from water by means of natural or artificial zeolites. They found that similar results were obtained with the natural and artificial substances, but that the latter were more active; that a given quantity of manganese sulphate was most effectively removed from dilute solution made to filter slowly through a bed of the silicate; that the presence of the salts of other bases in solution was unfavourable to the absorption of manganese; and that by subsequent treatment of the silicate with solutions of salts such as ammonium chloride, in order to revivify it, the whole of the absorbed manganese was not removed, but was found to be present partly as hydrated peroxide, which, on a large scale, tended to obstruct the filter beds.

The patents granted to R. Gans and the J. D. Riedel A.-G. in 1909 (French Patent 405,990, July 17, 1909; English Patent 21,184, Sept. 16, 1909; and U.S. Patent

951,641, March 8, 1910) contain claims for a process for removing iron and micro-organisms from water. It is stated that the process consists in treating the water with insoluble higher oxides of manganese with the co-operation of natural or artificial zeolites (*cf.* German Patents 145,797 and 154,792). The claim is made that if a calcium-zeolite is treated with a solution of a manganous salt, a manganese zeolite is formed, which, on treatment with a solution of calcium permanganate, yields a product consisting of the higher oxides of manganese distributed in a fine state of division throughout a calcium-zeolite. According to Gans (*Chem. Ind.*, xxxii., 197), 450 kgms. of calcium-zeolite were found to be changed, by washing with manganous chloride solution, to manganese-zeolite; treatment with a calcium manganate solution converted the latter into calcium-zeolite again. On filtering the water to be treated through this material, the iron is said to be rapidly oxidised and removed, and the bacteria and organic matter destroyed; any manganese present in the water is also said to be removed. In later patents to the same parties (French Patent 409,006, Nov. 13, 1909; English Patent 26,842, Nov. 18, 1909; and U.S. Patent 960,887, June 7, 1910), the water to be softened is treated with barium, calcium, or magnesium hydroxide, and sodium hydroxide or carbonate, according to the nature of the hardness, and then filtered through a layer of a natural or artificial zeolite.

When a water containing manganese salts in solution is passed through a filtering bed composed of a zeolite impregnated with higher oxides of manganese the manganese is separated in the form of a mud. It was found in practice as early as 1907 that if this mud was not removed from the filter, it eventually formed small porous particles which did not interfere with the filtering capacity of the bed, but, in fact, increased its efficacy with regard to the removal of manganese from water (see German Patent 220,609, Oct. 28, 1908, of the J. D. Riedel A.-G.). However, when revivification was attempted—*i.e.*, on the bed containing manganese mud—the manganese retained was found to be an obstruction to rapid filtration.

Natural stones, such as trass, phonolite, porphyry, leucite, trachyte, sodalite, and mica, are also employed in making filters through which the water to be treated is passed. These minerals are used either directly, if they have been hydrated naturally, or after they have been treated with steam under pressure; but we are not aware of their application in the place of artificial zeolite.

Two investigations have recently been published on "Permutite." Anders (*Woch. f. Brau.*, xxviii., 78) conducted laboratory experiments with the product for the softening of water. His results showed that "Permutite" is applicable for the softening of feed-waters, but not for mash-waters because it takes up sodium salts. He found that a "Permutite" filter may be completely regenerated by the use of a sodium chloride solution. Kolb (*Chem. Ztg.*, xxxv., 1393, 1410) also investigated the application of "Permutite" to the softening, as well as the purification, of water. He made experiments, both by shaking and by filtration, as to the interchange occurring between "Permutite" and the chlorides of calcium, magnesium, and potassium, and found that the soda of the "Permutite" was replaced by the bases of the salts added in molecular proportions. He also ascertained that the "Permutite" could be regenerated by treating the used substance with sodium chloride, and that iron and manganese, as well as the alkaline earth metals, could be removed from solution. Kolb stated that with a filter formed of "Permutite," complete softening of water could be effected, but the water must not contain acid or suspended matter. In the case of a muddy water, in addition to blocking the pores of the filter, the mud coated the grains of the filtering material with inert matter, and prevented the desired chemical reactions. Kolb considered the regeneration of the "Permutite" by a solution of sodium chloride to be of industrial importance, since it would enable the same filter to be used for an indefinite period. According to his

findings, the richness of the treated water in sodium salts is not detrimental to boiler-feed water.

It would seem that "Permutite," to be of value for technical uses, must be of a granular or leafy, easily porous character, such as is obtained by melting together the constituents in definite proportions. The amount of clay is calculated according to the amount of bases. Gans considers that the composition of an ideal zeolite,  $2\text{SiO}_2 \cdot \text{Al}_2\text{O}_3 \cdot \text{Na}_2\text{O} \cdot 6\text{H}_2\text{O}$ , should be approached.—*Journal of Industrial and Engineering Chemistry*, iv., No. 4.

## A NEW VOLUMETRIC METHOD FOR THE DETERMINATION OF MERCURY.

By GEORGE S. JAMIESON.

AMONG the methods that have been proposed for the volumetric determination of mercury, the titration in nitric acid solution by means of ammonium thiocyanate (Cohn, *Ber.*, xxxiv., 3502; also Rupp, xxxv., 2015), according to Volhard's method for silver, while it appears to be very accurate, is not generally applicable because it cannot be used in the presence of chlorides. The method of Rupp (*Ber.*, xxxix., 3702) consists in adding potassium iodide and an excess of sodium hydroxide to any mercuric solution, then precipitating the finely divided metal by means of formaldehyde, and, after acidifying with acetic acid, dissolving the metal with standard iodine solution and titrating back with sodium thiosulphate. This method is simple and rapid, and while it seems to be a good one for small quantities of mercury, my experience with it is that it gives seriously low results with amounts of mercuric chloride as large as 0.1 to 0.2 gm. Hempel's method (Sutton, 10th edition, p. 263), which consists in titrating mercurous chloride (or iodide) with iodine and thiosulphate, is undoubtedly very accurate, if it is used with proper precautions to completely dissolve the mercurous chloride in the iodine solution (Smith, *CHEMICAL NEWS*, cv., 14).

The method to be described is based upon the titration of mercurous chloride with potassium iodate in the presence of 15 to 20 per cent of actual hydrochloric acid and a small volume of an immiscible solvent, such as chloroform. This general method of titration is the well known one of L. W. Andrews (*Journ. Am. Chem. Soc.*, 1903, xxv., 756), but as far as is known it has not been applied previously to the titration of mercurous chloride. It has the advantage over Hempel's method in requiring only a single very stable volumetric solution, instead of two solutions which cannot be preserved for a long time unchanged, while the method of titration appears to be no less exact. It is to be observed that the iodate titration cannot be applied to mercurous iodide without the employment of an entirely different factor, since the iodine would affect the results.

It has been found that mercurous chloride reacts with potassium iodate according to the theoretical requirements of the equation—



In order to test the method a solution of potassium iodate was standardised with pure sublimed iodine, using Andrews' titration under the same conditions as are described beyond for the mercurous chloride titration.

|         | Iodine taken. | KIO <sub>3</sub> used. | Wt. of I for 1 cc. |
|---------|---------------|------------------------|--------------------|
|         | Grm.          | Çc.                    | Grm.               |
| A ..    | 0.1003        | 11.8                   | 0.00848            |
| B ..    | 0.1998        | 23.6                   | 0.00846            |
| Average | —             | —                      | 0.00847            |

Since the reaction in the case of iodine is represented by the equation  $4\text{I} + \text{KIO}_3 + 6\text{HCl} = \text{KCl} + 5\text{ICl} + 3\text{H}_2\text{O}$ , the

strength of the potassium iodate solution was 1 cc. = 0.01572 gm. of HgCl.

For the following titrations a sample of pure mercurous chloride which had been dried at 130–135° C. for several hours and well pulverised was used. The titrations were carried out in a glass-stoppered bottle of 250 cc. capacity in the presence of 20 cc. of water, 30 cc. of concentrated hydrochloric acid, and 6 cc. of chloroform, with thorough shaking of the closed bottle between the additions of the potassium iodate solution. As is usual in such titrations, the chloroform globule at first increases in iodine colour and then this colour is gradually removed. The end-point is the disappearance of this violet colour. It was observed that dried mercurous chloride reacts more slowly in this operation than the precipitated substance which was titrated without drying in some of the experiments to be described beyond, so that in this case very thorough shaking and occasional crushing of the lumps with a glass rod were required. The following table gives the results of the titrations:—

|      | HgCl taken.<br>Grm. | KIO <sub>3</sub> .<br>Cc. | HgCl found.<br>Grm. | Error.<br>Grm. |
|------|---------------------|---------------------------|---------------------|----------------|
| I.   | 0.4999              | 31.80                     | 0.4999              | 0.0000         |
| II.  | 0.5000              | 31.80                     | 0.4999              | 0.0001         |
| III. | 0.5005              | 31.80                     | 0.4999              | -0.0006        |
| IV.  | 0.6001              | 38.15                     | 0.5997              | -0.0004        |
| V.   | 0.4999              | 31.80                     | 0.4999              | 0.0000         |

The results show a very satisfactory agreement among themselves and with theory.

Since most kinds of organic matter do not interfere with this method of titration, it is applicable to various mixtures containing calomel. It was tried with calomel tablets containing milk-sugar, after pulverising several tablets to obtain a uniform mixture. Quantitative determinations of the calomel were also made by treating portions of the substance with water slightly acidified with hydrochloric acid and weighing the washed and dried residue. The following results were obtained:—

| Substance taken (grm.). | KIO <sub>3</sub> used (cc.). | HgCl found (per cent). |
|-------------------------|------------------------------|------------------------|
| 0.4811                  | 16.50                        | 53.91                  |
| 0.6783                  | 23.25                        | 53.89                  |
| 0.1976                  | gravimetric                  | 53.94                  |
| 0.5694                  | "                            | 54.00                  |

The method was applied also to the determination of mercury in a mercuric compound by converting the latter into mercurous chloride and then titrating. For this purpose weighed portions of mercuric chloride were dissolved in warm water with the addition of a few drops of hydrochloric acid; an excess of phosphorous acid solution was then added, and after thorough stirring the precipitate in each case was allowed to settle for about twelve hours. It was then collected on a filter-paper and well washed with cold water. The precipitate with the paper was put into the titration bottle, and any precipitate adhering to the beaker and stirring rod was collected by wiping with a piece of filter-paper, and also put into the bottle. The titrations were carried out as previously described, with the following results:—(1 cc. KIO<sub>3</sub> = 0.13354 gm. Hg)

| No.  | HgCl <sub>2</sub> taken.<br>Grm. | KIO <sub>3</sub> sol. used.<br>Cc. | Hg found.<br>Grm. | Hg calculated.<br>Grm. | Error.<br>Grm. |
|------|----------------------------------|------------------------------------|-------------------|------------------------|----------------|
|      |                                  |                                    |                   |                        |                |
| I.   | 0.3934                           | 21.7                               | 0.2898            | 0.2904                 | -0.0006        |
| II.  | 0.3107                           | 17.2                               | 0.2297            | 0.2294                 | +0.0003        |
| III. | 0.4903                           | 27.1                               | 0.3619            | 0.3619                 | 0.0000         |
| IV.  | 0.3315                           | 18.3                               | 0.2444            | 0.2447                 | -0.0003        |
| V.   | 0.3407                           | 18.8                               | 0.2511            | 0.2515                 | -0.0004        |

The results show that the method is an accurate one.—*American Journal of Science*, xxxiii., No. 196.



THE ISOLATION OF CREATININE FROM SOILS.\*

By EDMUND C. SHOREY.

In the course of investigations into the nature of the organic constituents of soils a crystalline organic compound was isolated and identified as creatinine.

Reactions indicating the presence of this compound were first observed in a solution of a portion of the soil organic matter obtained in the following manner:—The soil was treated with 2 per cent sodium hydroxide solution for half an hour, and then without separation of the alkaline extract from the soil, acetic acid in slight excess was added and the acid solution filtered from the soil and precipitate formed. The acid filtrate was neutralised with sodium hydroxide, and, without filtering, a solution of lead acetate added and the precipitate formed, separated by filtration. On the addition of ammonia to the filtrate a further precipitate was produced, which was filtered off, washed, and decomposed by hydrogen sulphide. The filtrate from lead sulphide was concentrated to a small volume, and was found to give the Jaffé, Weyl, and Salkowski colour reactions for creatinine.

It was further found that if the filtrate from the neutral lead acetate precipitate was made alkaline with sodium hydroxide instead of ammonia, and the resulting precipitate decomposed and concentrated, the colour reactions were obtained more strongly, indicating a more complete precipitation of the creatinine by this means.

From the known behaviour of creatinine when treated with lead acetate in alkaline solution it was evident that neither of the methods of precipitation mentioned would result in complete separation of the creatinine present, and for the isolation of this compound recourse was had to another method.

The method by which creatinine was first isolated from soils, and already noted elsewhere (*Science*, 1911, xxxiii., 310), was to apply to an alkaline soil extract a method recommended by Balke (*Fourn. Prakt. Chem.*, 1893, [2], xlvii., 537) for the separation of purine bases, and used for that purpose in the Bureau of Soils Laboratory (*Bull.* 74, Bureau of Soils, 1910, p. 41; *Fourn. Biol. Chem.*, 1910, viii., 391). This method depends on the fact that when there is precipitation of cuprous oxide from Fehling's solution by a reducing compound, purine bases and some related compounds combine with the cuprous oxide and are found in the precipitate. Creatinine behaves in this way, as was first pointed out by Masche (*Zeit. Anal. Chem.*, 1878, p. 134).

The method as applied to the isolation of creatinine from soils was carried out as follows:—An alkaline extract of the soil, made by treatment for a short time with 2 per cent sodium hydroxide, was made exactly neutral with acetic or sulphuric acid and filtered. The neutral filtrate was heated to boiling and a little glucose added, and then Fehling's solution, slightly in excess of that required by the glucose present. The precipitate formed was separated by filtration, well washed, and decomposed by hydrogen sulphide. The filtrate from the copper sulphide was concentrated to a small volume under reduced pressure, a small quantity of a concentrated solution of zinc chloride and a little sodium acetate added, and the whole allowed to stand several days. Within a few hours crystals began to form, and in forty-eight hours these were observed to have the characteristic appearance of creatinine zinc chloride. The crystals were separated from the mother-liquor by filtration, or, when the quantity of material was very small, by placing the whole mass on a porous plate. After separation the crystals were washed with a little cold water, suspended in water, and boiled with some freshly precipitated lead hydroxide, filtered, and the filtrate concentrated to a small volume; on standing a short time crystals formed having the appearance, solubility, and colour reactions of creatinine.

From another portion of the same soil from which creatinine had been obtained by the method just outlined, creatinine was also obtained by alcoholic extraction. About 100 grms. of air-dried soil were extracted in a Soxhlet extractor for seven hours with 95 per cent alcohol. The alcohol was removed from the coloured extract so obtained by evaporation, water being added to keep the volume constant. The aqueous solution was filtered from resinous and fatty matter and evaporated to a small volume under reduced pressure. The concentrated solution gave all the colour reactions for creatinine strongly, and on treatment with zinc chloride gave, after standing two days, crystals of the characteristic creatinine zinc chloride.

Creatinine was also obtained from the same soil by simple extraction with water. About 5 kilograms of soil were extracted with cold distilled water in a percolator until 8 litres of extract had been obtained. This was concentrated to about 100 cc. by evaporation under reduced pressure, and filtered from a small quantity of insoluble matter present. The solution so obtained gave all the colour reactions for creatinine strongly, and on treatment with zinc chloride, crystals of the characteristic creatinine zinc chloride were formed. From these, by treatment with lead hydroxide in the manner already described, crystalline creatinine was obtained.

Creatinine in water solution gives a number of colour reactions that have been depended on largely as indicating or proving the presence of this compound in fluids such as urine.

**Jaffé's Reaction.**—If a solution of creatinine be made alkaline with sodium hydroxide and then a few drops of picric acid solution added, a red colour is formed (*Zeit. Phys. Chem.*, 1896, x., 399). The colour, which is similar to that of a concentrated solution of potassium dichromate, becomes orange on dilution. A quantitative colorimetric method for determining creatinine based on this reaction has been devised by Folin (*Zeit. Phys. Chem.*, 1904, xli., 223) and has been almost universally adopted in determining the quantity of this compound in urine. In the use of this reaction for either qualitative or quantitative purposes the absence of other compounds that give a similar colour or that give a colour that would obscure the one given by creatinine must of course be assured. In urine the only compound of this nature likely to be present is acetone, the presence of which can, of course, be easily determined. In solutions or extracts, however, containing soil organic matter there is the possibility of other compounds that may simulate or obscure the colour given by creatinine, but whose presence can not be definitely determined, because of lack of sufficient methods. Levulinic acid and furfural both give the Jaffé reaction strongly, and while neither have been definitely identified as present in soils, there are some indications of the presence of the former, and the latter might very easily be present or formed in soil extracts at some stage in the operation.

**Weyl's Test.**—A watery solution of creatinine to which a small quantity of a solution of sodium nitroprusside has been added gives on the addition of sodium hydroxide a red colour, which soon changes to yellow (*Ber.*, 1878, xi., 2175; Arnold, *Zeit. Phys. Chem.*, 1906, xlix., 397). As with the Jaffé reaction, the presence of certain other compounds may interfere with the use of this test either by giving a colour that obscures the one given by the test, or giving a similar one. Levulinic acid gives under the conditions of this test a colour similar to that given by creatinine, and this test with others has been used to establish the presence of levulinic acid in the decomposition products of nucleic acid (Inouye, *Zeit. Phys. Chem.*, 1904, xlii., 116). Furfural and the products resulting from heating pentose-yielding material with acid give a similar colour, although in no case is the fading of the red colour to yellow as pronounced as with creatinine. The dark purple colour given by sulphides in the presence of sodium nitroprusside and sodium hydroxide would, of course, obscure the colour given by creatinine, and, as was noted

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in the case of Jaffé's reaction, there are probably in soil extracts unknown compounds that give either a similar colour or one that would obscure the one given by creatinine.

**Salkowski's Reaction.**—If the yellow solution resulting from Weyl's test be acidified with acetic acid and then heated, the solution turns green, then blue, and Prussian blue is precipitated, if much creatinine is present (*Zeit. Phys. Chem.*, 1880, iv., 133; 1885, ix., 127). Both levulinic acid and furfural give the final blue colour and precipitate, but in the case of levulinic acid the solution after the addition of acetic acid and before heating is purple. The reagents alone will give the final blue colour and precipitate if the solution before acidifying be allowed to become warm.

Since soil extracts or solutions prepared from them may contain compounds that are known to give colour reactions similar to those given by creatinine, and since there is the possibility of the presence of others as yet unknown, it is evident that results obtained with the colour tests usually considered indicative of the presence of creatinine can not be considered conclusive proof of the presence of this compound in the soils from which the soil extracts were prepared.

When indications of the presence of creatinine are obtained by any of the colour tests just described, this can best be confirmed and established by the preparation of the creatinine zinc chloride  $(C_4H_7ON_3)_2ZnCl_2$ . This salt, almost insoluble in alcohol and difficultly soluble in water, is formed when concentrated solutions of creatinine and zinc chloride are brought together in the absence of free mineral acids, a condition usually obtained by the addition of a little sodium acetate. When any large quantity of creatinine is treated in this way there is immediate precipitation, but when small quantities are being dealt with precipitation does not begin for several hours and is not complete for several days. The crystals of this salt are quite characteristic in form, although this form is so modified by the concentration of the solution, the presence of other substances, and other conditions that they appear to differ widely. A study of the form assumed when the crystals first appear, and of their growth, and of the form assumed on re-crystallising, soon results in familiarity with the characteristic appearance, so that the compound can be readily identified, no matter what form it may assume. Usually it appears in balls with radiating structure, due to their being made up of fine needles. Under other conditions its first appearance may be in star-like plates which eventually assume the form of bunches of radiating needles or plates. If the crystallisation is slow, the plates may grow to a well developed form. Under still other conditions the radiating needles are bunched in tufts rather than balls. This last form is the one assumed by the pure compound when a concentrated solution is cooled rapidly.

When sufficient creatinine zinc chloride can be prepared pure, its identification by the method of preparation, solubility, and crystalline form may be supplemented by analysis, although once familiarity with the characteristic behaviour and appearance of this compound is acquired, this is not essential. A preparation of creatinine zinc chloride made from an alkaline soil extract in the manner already described was purified by re-crystallisation, dried on a porous plate, and then in a desiccator, and nitrogen and zinc oxide determined in the following manner:—A portion of the creatinine zinc chloride, 0.3600 gm., was digested with a small quantity of sulphuric acid and a little potassium sulphate, as in the Gunning modification of the Kjeldahl method for total nitrogen. The resulting solution was made alkaline with sodium hydroxide and distilled into standard acid in the usual manner. After the removal of the ammonia by distillation the solution was made acid with acetic acid and the zinc in solution precipitated by hydrogen sulphide, the zinc sulphide collected, the precipitate and filter-paper treated with nitric acid, dried, and

carefully ignited and weighed as zinc oxide. The analysis gave the following figures:—

|                                          | N.    | ZnO.  |
|------------------------------------------|-------|-------|
| Calculated for $(C_4H_7ON_3)_2ZnCl_2$ .. | 23.16 | 22.45 |
| Found .. .. .                            | 23.22 | 22.31 |

(To be continued)

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

Ordinary Meeting, May 16th, 1912.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"General Theory of Colloidal Solutions." By W. B. HARDY, F.R.S.

The physical properties of colloidal solutions prove them to be heterogeneous fluids. If the colloid particles are regarded as a stage in the appearance of a second fluid phase the variations of the energy of the particles with the radius are of predominant importance. If we could assume, for instance, that the tension of the interface varied with the radius as the tension of a free film of fluid was found to vary with the thickness of the film by Renold and Rücker, globules of certain dimensions would alone be stable. It is pointed out, however, that at present there is no adequate basis in experiment or theory for regarding the peculiarities of soap films, themselves a colloidal form of matter, as the property of films or minute spheres of matter in general.

"Tension of Composite Fluid Surfaces and the Mechanical Stability of Films of Fluid." By W. B. HARDY, F.R.S.

In order to gain further information as to the variations of surface energy with variations in the thickness of a film, the tension and mechanical stability of the surface of water on which a known impurity was allowed to spread has been investigated. It was found that the effect of the impurity depended upon its chemical nature. Substances of great chemical stability, such as the higher paraffins, refuse to spread at all, and only slightly lower the tension of water. Esters—such as glycerides—produce a great fall of tension, and an exceedingly thin film of the order of  $2\mu$  thick suffices. It is suggested that the great activity of esters is due to their being partly decomposed at the interface with the production of a contact difference of potential between the film and the water.

"Formation of a Heat-reversible Gel." By W. B. HARDY, F.R.S.

In the course of his study of the cyclo-pentanes, Dr. Ruhemann has synthesised a substance which forms gels with apparently any solvent (alcohol, ether, carbon tetrachloride, carbon bisulphide, aldehyde, glacial acetic acid, &c.). A remarkable feature is that gelation occurs as readily in associating as in non-associating solvents. The gels have a peculiar structure owing to the fact that gelation starts from nuclei and only gradually involves the whole mass.

"Studies on Enzyme Action. XVI.—The Enzymes of Emulsin (II); Prunase, the Correlate of Prunasin." By H. E. ARMSTRONG, F.R.S., E. F. ARMSTRONG, and E. HORTON.

Evidence has been adduced in previous studies of the series that the diglucoside amygdalin is resolved into glucose, benzaldehyde, and hydrogen cyanide by two distinct enzymes present in the emulsin prepared from the almond fruit, one (amygdalase) serving to resolve it into glucose and  $\delta$ -mandelonitrile glucoside or prunasin, the



other to convert this latter compound into glucose, benzaldehyde, &c. Amygdalase is known to occur in certain yeasts unaccompanied by the second enzyme. It is now shown that the second enzyme occurs in the leaf of the almond and of other species of *Prunus* from which prunasin, but not amygdalin, may be separated; it is proposed to term this enzyme *prunase*. Apparently, the two enzymes are always present in the fruit in association with amygdalin, but amygdalin is not known to occur in the leaf, and the leaf enzyme, as a rule, has little action on amygdalin.

"Studies on Enzyme Action. XVII.—Enzymes of the Emulsin Type (II.): The Distribution of  $\beta$ -Enzymes in Plants." By H. E. ARMSTRONG, F.R.S., E. F. ARMSTRONG, and E. HORTON.

A method of general application is described by which the enzymic activity of plant materials may be determined. It has been applied to the study of the distribution in plants of enzymes capable of acting on the glucosides linamarin, prunasin, salicin, arbutin, and amygdalin.

"Studies on Enzyme Action. XVIII.—Enzymes of the Emulsin Type (III.): Linase and other Enzymes in Linaceæ." By H. E. ARMSTRONG, F.R.S., and J. VARGAS EYRE, Ph.D.

The method developed in the previous communication has been applied to various species of Linaceæ. The family is found to be divisible into two groups—one of these, which apparently includes all species similar in habit to *L. usitatissimum*, having blue, white, or red flowers, contains the cyanophoric glucoside linamarin and the corresponding enzyme linase. The second group, which comprises the yellow-flowered species of arboreal habit (*L. arboreum*, *L. flavum*, &c.), apparently contains neither glucoside nor enzyme. One important outcome of the inquiry is the proof that whereas the enzyme extracted from *Phaseolus lunatus* is about equally active towards linamarin and prunasin, that present in *Linum* is much less active towards the latter. It is therefore not improbable that linase is usually accompanied by prunase, and itself without action on prunasin.

"Reflex Rhythm Induced by Concurrent Excitation and Inhibition." By ALEXANDER FORBES, B.Sc., Harvard.

"Factors in Rhythmic Functions of the Nervous System." By T. GRAHAM BROWN.

# PHYSICAL SOCIETY.

Ordinary Meeting, May 10th, 1912.

Prof. A. SCHUSTER, F.R.S., President, in the Chair.

A PAPER ON "The Generation of Electricity by Carbon at High Temperatures," by Dr. J. A. HARKER, F.R.S., and Dr. G. W. C. KAYE, was read by Dr. HARKER.

The experiments described owe their origin to some contamination phenomena which were encountered when tubes of refractory rare earths were baked in carbon-tube resistance furnaces at temperatures from 1500° C. upwards. It was found that the tubes often had their outer surfaces carbonised to an appreciable depth, while the inner surfaces, though freely exposed, were much less attacked. The blackening was presumably caused by particles shot from the carbon walls of the furnace with velocity high enough to penetrate the refractory material after crossing a few mm. of air at atmospheric pressure.

The preliminary experiments on the nature of these particles were carried out by the use of two insulated exploring electrodes of carbon inserted into an alternating-current furnace. They were connected externally to a battery of cells and the potential-current curves were determined for the electrode gap in the furnace at a number of

temperatures. No appreciable current could be detected at temperatures below about 1400° C., but as the temperature rose it was found that quite small E.M.F.s gave rise to steady currents of relatively enormous magnitude.

For example, with 8 volts, currents up to 10 amperes have been obtained at a temperature of about 2500° C.

The relation between current and temperature was found to be of an exponential character.

The magnitude of the currents made it evident that the atmosphere of the furnace was ionised to an unusual degree at high temperatures, and the authors were led to try the effect of temperature alone in the absence of any applied potential. Accordingly the battery was cut out, and while one of the electrodes remained stationary within the furnace the other could be suddenly displaced to a colder or hotter part of the furnace. The resulting difference of temperature manifested itself as a transient current in the circuit, which in some cases amounted to 2 amperes. The current died away when the two electrodes attained the same temperature.

In the apparatus shown the movable electrode was moved in and out of the hot region of the furnace by means of a clockwork mechanism. The pulsating electric current thus produced was large enough at high furnace temperatures to light up a nest of small glow lamps, the illumination waxing and waning as the movable electrode moved in and out. The experiment has been modified in later work by keeping both electrodes stationary and water cooling one of them. The cold electrode was made up of a brass tube, which in some cases was provided with a carbon sleeve. A continuous current can thus be generated. Its direction is such as would be produced by a discharge of negative particles from the hot electrode. As before, no potential is applied. At the lower temperatures small positive currents have also been detected; at high temperatures negative currents up to nearly an ampere have been measured. The whole of the experiments were conducted at atmospheric pressure, and almost entirely with low-voltage alternating-current furnaces.

## DISCUSSION.

Mr. G. D. WEST thought that it seemed from the above experiments, that in a carbon filament lamp, if run at a high enough temperature, more current might be carried by the ionised gas than by the filament.

Prof. C. H. LEES remarked that the authors declined to give any theory of the effect they had observed. Was the emission one of electrons or was some chemical action taking place? Some papers before the German Physikalische Gesellschaft had recently cast doubt on the emission of electrons from heated bodies observed by H. A. Wilson and O. W. Richardson, and it had been pointed out that a chemical reaction would follow Richardson's formula, which afforded therefore no proof that the effect was due to electrons.

Dr. ERSKINE MURRAY asked if the authors had found the emission to remain steady for several hours. The phenomenon was similar to that of the valves used in wireless telegraphy.

The PRESIDENT said he had listened with considerable interest. The authors had done on a large scale what had been done on a small scale a few years ago. He doubted the emission being electrons, and thought that some electrochemical effect should be sought for.

Dr. HARKER, in reply, stated that the effect was not chiefly a chemical effect as it was the same whether the gas in the furnace was H<sub>2</sub> or N<sub>2</sub>, nor did it matter what the carbons were made of. Specially pure carbons gave phenomena of just the same order of magnitude.

Dr. KAYE, in reply, stated that the feature which differentiated their experiments from others was that the effect occurred at atmospheric pressure and not *in vacuo*. It was hardly likely at this pressure that the effect could be confined to electrons, as the mean free path of such would be very small. The effect might be due to the trans-

erence of carbon itself, probably in ultra-microscopic particles and not molecules. When a cold tube was used for one of the electrodes it was found in half an hour to be coated with a deposit of carbon. There was no likelihood that the effect would decay with the time, as it had been kept constant for over three hours. It was also not necessary to use electric heating in the furnace. Heating by thermit and Méker gas furnaces both gave the same results.

A paper by Mr. S. BUTTERWORTH on "*A Method of Measuring Small Inductances*" was read by Mr. A. CAMPBELL.

The author shows how Anderson's method may be modified so that, while still retaining the usual standards of capacity, very small inductances may be measured.

As in Anderson's method, balance is attained by a simple resistance adjustment.

The conditions of maximum sensibility are indicated and experimental results are quoted in which an inductance of 20 microhenries is compared with a capacity of 0.1 mfd.

The method may also be employed to compare a very low capacity with the usual mica standards of capacity.

#### DISCUSSION.

Dr. A. RUSSELL took it that the author had assumed no iron in the circuit in obtaining his formula.

Mr. A. CAMPBELL pointed out that the author obtained his balance by means of a vibration galvanometer, so the method would correctly give the apparent self-induction at that particular frequency.

Dr. W. H. ECCLES pointed out that the method would be rarely used for coils with iron cores since it was for small inductances. Since the periodicity of the alternating current did not occur in the equations for equilibrium the method could, if all the resistances were independent of the frequency, be used with an interrupted current and a telephone.

The PRESIDENT remarked that all who had had occasion to try it knew how difficult it was to measure a small self-induction, and would therefore welcome Mr. Butterworth's paper.

A paper on "*The Conversion of Starch into Dextrin by X-Rays*," by H. A. COLWELL, M.B., and S. RUSS, D.Sc., was read by Dr. RUSS.

When solutions of starch are irradiated for several hours by X-rays of moderate penetrating power, the opacity and viscosity of the solutions are markedly diminished. These physical changes are attended by chemical changes; there is a partial conversion of the starch into soluble starch and dextrin. A quantitative estimation of the amount of dextrin formed after the starch solution had been irradiated for eight and a-half hours showed that it corresponded to about 5 per cent of the amount of starch initially present.

When solutions of dextrin were subjected to a similar exposure of X-rays, no conversion of this substance into glucose was obtained. From the fact that starch may be converted into dextrin by hydrolysis, a simple explanation of the effect would be afforded if water were decomposed by X-rays. From the negative results obtained by Kernbaum on these lines, however, it seems as if the effect were more likely attributable to a direct action upon the starch molecules, either by the X-rays or the secondary rays which they produce.

#### DISCUSSION.

The PRESIDENT thought the paper one of considerable importance as definitely proving the chemical effect of X-rays.

Dr. A. D. WALLER also expressed his interest in the paper.

#### FARADAY SOCIETY.

Ordinary Meeting, April 23rd, 1912.

Sir ROBERT HADFIELD, F.R.S., in the Chair.

#### GENERAL DISCUSSION ON THE MAGNETIC PROPERTIES OF ALLOYS.

THE CHAIRMAN in his introductory remarks extended, in the first place, a hearty welcome to those visitors who had come from abroad to take part in the discussion. He then gave a brief account of the early work in this field, referring more particularly to the non-magnetic ferro-alloys with which he had been associated. He pointed out how magnetic properties depended on heat treatment as well as on composition, and showed a bar of manganese steel which was magnetic at one end and non-magnetic at the other. To illustrate the necessity of working carefully through whole series of alloys before any conclusions could be arrived at, he remarked that whereas a 5 per cent manganese steel was very brittle and magnetic the addition of 14 per cent nickel rendered the steel both very tough and non-magnetic.

The first paper was read by Geheimrat Dr. E. GÜMLICH (Berlin), and dealt with "*The Magnetic Properties of Iron-carbon and Iron-silicon Alloys*." The photomicrographs shown were the work of Prof. P. Goerens.

The experiments conducted by the Physikalisches Reichsanstalt, on which the author reported, were commenced a few years ago on the instigation of German technologists, and with the joint assistance of the Verband Deutscher Elektrotechniker, some German ironmasters, and the Metallurgical Laboratory of the Technical High School at Aachen (Profs. Wüst and Goerens).

The experiments aimed at investigating the relations between the magnetism of iron alloys and their chemical composition and thermal treatment. Although the researches are by no means completed, the Reichsanstalt would like to communicate some of the results obtained to the Faraday Society as a contribution to this discussion. The results concern magnetisation up to saturation, coercive force, remanence, and the electric resistance of the alloys iron-carbon and iron-silicon.

Carbon, it is well known, behaves in these alloys in very different ways according to the thermal treatment (slow or rapid cooling) it has undergone, and the differences can be traced in the physical properties, as well as in the structure (cementite, pearlite, martensite, temper-carbon) which is characterised by the presence of the carbon. The carbon which is dissolved in the iron has the strongest influence upon the magnetic properties, and it has resulted that the coercive force of these alloys increases proportionally as the dissolved carbon, while the remanence decreases. These conclusions are important for the manufacture of permanent magnets. The carbon present as impurity plays, however, also an exceedingly important and very disturbing part in the manufacture of dynamo steel, transformer iron, &c., which are to be particularly soft magnetically, because the carbon decreases the permeability and increases the hysteresis loss. Since carbon cannot altogether be eliminated in practice, the manufacture has to attempt to render it innocuous so far as possible, and the author's experiments demonstrate that a considerable addition of silicon has this effect.

In 1890 Barrett, Brown, and Hadfield published experiments which proved that the addition of silicon to iron diminishes the electric conductivity without impairing the magnetic properties. On the strength of these observations, the Reichsanstalt induced German ironworks to make transformer sheets out of silicon-iron in order to reduce the Foucault-current losses in the transformers. The realised improvement was much greater than was expected; for it resulted that the magnetic properties were generally improved, and the hysteresis losses in particular much reduced. The part which the silicon plays in this improvement is not clear yet. The experi-



ments of the Reichsanstalt show that the influence is not a direct one, for in that case the magnetisation should increase with increasing silicon percentage, particularly in fields of high intensity. The saturation value should hence increase whereas it decreases, just as if the silicon were a non-magnetic addition to the iron merely acting by reducing the effective cross-section of the iron. The influence of silicon is hence indirect, and it seems in some way to counteract and to eliminate the detrimental effect of the carbon. For it would appear that on continued heating the carbon cannot remain dissolved in the iron, being transformed partly into the less detrimental cementite and partly into the altogether harmless temper-carbon.

The microphotographs which Prof. Goerens (Aachen) has taken of the magnetically examined specimens are in very satisfactory agreement with the results of the studies of the alloys of iron-carbon and iron-silicon.

Prof. E. WEDEKIND (Strasbourg) then read his paper on "*Relations between the Magnetism and the Stoichiometrical Constitution of Chemical Compounds.*"

The present state of our knowledge concerning the dependence of the magnetic properties of compounds upon the nature and the number of the elements entering into combination may be summed up in the following statements:—1. The magnetism of simple chemical compounds, derived from a ferromagnetic metal or a metal of latent magnetism, is a well-defined molecular property of the compound which is connected with the stoichiometrical composition, or with the constitution of the compound. 2. The magnetism of simple compounds of ferromagnetic metals is throughout essentially feebler than that of the metal, so far as independent representations of valencies are concerned. 3. Simple compounds of metals of latent magnetism (Mn, Cr, V, presumably also Ti) are, as a rule, more strongly magnetic than the metals; the maximum intensity depends upon the stoichiometrical composition, however, particularly in cases where several compounds exist of the same components. Manganese has a maximum in its trivalent state with regard to the elements which can themselves be trivalent, *i.e.* in the atomic ratio 1:1. Some of these compounds behave like permanent magnets. 4. With the independent oxides of manganese, chromium, and vanadium the susceptibility appears to be a function of the metal percentage, in the case of the vanadium sulphides a linear function of the sulphur percentage; the magnetic susceptibility is thus dependent upon the valency of the metal in the respective compound. 5. So-called mixed oxides or sulphides which do not represent uniform valencies are with all the metals more intensely magnetic than the independent classes of compounds. There is a correlation with the acid nature of the one component, which always represents the higher oxide. Such a compound is always graphically revealed by a sharp bend in the curve. 6. The magnetic susceptibility decreases, on the whole, with decreasing atomic weight of the chief metal. Several manganese compounds are still ferromagnetic. Of chromium compounds only the two mixed oxides already referred to are still ferromagnetic; none of the vanadium compounds are any more decidedly ferromagnetic. The minimum is probably reached in titanium, which stands to the left of vanadium, and in the titanium compounds which are now being investigated. The next element in succession, scandium, is already diamagnetic as oxide.

Dr. JAMES G. GRAY and Dr. ALEXANDER D. ROSS (Glasgow) presented a paper "*On the Magnetic Properties of a Variety of Special Steels at Low Temperatures,*" which was read by Dr. Ross.

Specimens of iron, carbon steels, silicon steels, chrome steels, &c., were tested at room temperature, and when immersed in boiling liquid air, in the conditions brought about by normalising, annealing, and quenching the metal at various temperatures. It was found that the effect of cooling the specimens was, in general, to diminish the permeability for low field strengths, and to increase it for

high fields. A magnetisation curve corresponding to  $-190^{\circ}\text{C.}$  lies initially below and finally above one corresponding to  $15^{\circ}\text{C.}$  This is shown to be in harmony with the theory of elementary magnets whose intensity of magnetisation and polar length varies with the temperature. It was found that, in general, the crossing point of the I-H curves corresponding to  $15^{\circ}$  and  $-190^{\circ}\text{C.}$  respectively, is higher the greater the amount of the added element present. This rule holds in any of the conditions mentioned above. The value of the magnetising force necessary to bring about crossing of the magnetisation curves for the material at  $15^{\circ}$  and  $-190^{\circ}\text{C.}$  is very low in the case of chrome steel. For a specimen of this variety of steel containing 1 per cent of chromium the curves crossed for a field strength of 8 c.g.s. units.

Cooling to the temperature of liquid air results in the coercive force being increased, and this effect is very pronounced in the case of materials which have been quenched. For high carbon steel in the quenched condition the coercive force at room temperature is 32; at  $-190^{\circ}\text{C.}$ , it is 50.

Dr. ALEXANDER D. ROSS also read a paper "*On the Magnetic Properties and Microstructure of the Heusler Alloys.*"

The paper describes a series of tests on ternary alloys of copper, manganese, and one of the elements aluminium, tin, antimony, and bismuth, and also on several magnetic binary alloys. Details are given of the method of casting and annealing the metal, and a description is given of a special form of magnetometer which was designed in order to increase the accuracy of the tests. The primary object of the magnetic tests was (1) to determine the magnetic quality of the alloys in the condition as cast, (2) to find the best thermal treatment for rendering the metal of good magnetic quality, (3) to test the variation of permeability with temperature, and (4) to investigate the effects of annealing and quenching the alloys at various temperatures. The Heusler alloys are improved by annealing at  $180^{\circ}\text{C.}$  The best duration of the annealing process varies from a few minutes to several hours, according to the composition of the specimen. It is found that the effect on the magnetic quality brought about by cooling these alloys to the temperature of liquid air is decidedly different from what is found in iron alloys. The magnetic experiments combined with thermal and microscopic tests have proved that the Heusler alloys are solid solutions probably consisting of  $\text{Cu}_3\text{Al}$  and  $\text{Mn}_3\text{Al}$  in the case of magnetic ternary alloys of copper, manganese, and aluminium. There is no indication of the occurrence of ternary compounds, and the experiments do not support the theory that the magnetic quality is due to a change brought about in the transformation temperature of manganese through its solution in copper or copper-aluminium.

A paper by Dr. S. HILPERT (Berlin) and Dr. E. COLVER GLAUERT (Sheffield) on "*The Magnetic Properties of Nickel and Manganese Steels with reference to their Metallographical Composition*" was read by Dr. COLVER GLAUERT.

A series of nickel and manganese steels (5 to 33 per cent nickel and 5 to 10 per cent manganese) were investigated, by quenching from various temperatures and other thermal treatment, and then quantitatively measured magnetically at room temperatures.

From the products so produced cooling experiments were carried out to  $-180^{\circ}\text{C.}$ , and the specimens were then re-heated in stages to the highest initial temperature employed, and similar magnetic investigations pursued. The following results were obtained:—

At high temperatures ( $1200^{\circ}\text{C.}$ ) compounds are produced which at room temperatures are strongly magnetic, the only exception being the 33 per cent nickel steel. This proves that the allotropic theory, which holds that magnetism rests entirely with alpha iron, is no longer tenable as regards these steels, since the slowly cooled steels are less magnetic than those quenched from high temperatures.

The 25 per cent nickel steel, which most commonly

occurs in practice when a non-magnetic alloy is required, was subjected to very close investigation, and a diagram produced showing the magnetic "life" of this steel for all temperatures, and showing the conditions under which its magnetism may vary between zero and maximum. This maximum is practically such as would be expected from a mixture of iron and nickel of the proportions found in the steel. In this steel two irreversible temperature hysteresis loops are found and shown in diagrammatic form. The 33 per cent nickel steel was found to be quite different to the other iron alloys, and it seems highly probable that steel of this composition must be regarded as a special compound.

Metallographic investigations prove that for these steels it is impossible to correlate any given structure with given magnetic properties. In this investigation sulphurous acid was used as the etching medium, and the structures obtained are different to those usually shown for nickel steels, being much more similar to those of meteoric iron.

The manganese steels were investigated in collaboration with W. Mathesius.

Dr. S. HILPERT and Dr. T. DIECKMANN presented a paper entitled "*The Magnetic Properties of the Compounds of Manganese with Phosphorus, Arsenic, Antimony, and Bismuth.*" This was also communicated by Dr. Colver-Glauret.

The magnet change points of these compounds were proved to be closely connected with the atomic weights of the substance compounded with the manganese.

The highest is that of MnBi (380° C.) and the lowest that of MnP (18° to 25° C.). If this latter is warmed in the hand, it no longer reacts with a magnet, but immediately does so if it is placed in cool water. This was experimentally demonstrated.

The following is a summary of a paper communicated by Dr. E. TAKE (Marburg) and Dr. F. HEUSLER (Dillenburg).

1. In order to account for the pronounced ferromagnetism of the Heusler alloys, aluminium, or tin-manganese bronzes, Guillaume assumes with Faraday that pure manganese exists in a strongly magnetic modification, which undergoes transformation at a very low temperature; this temperature is said to be raised by the addition of Al or Sn, so that the magnetism of these alloys becomes apparent. This hypothesis is not based upon facts, and the arguments are not sufficiently supported; it would, moreover, not explain the strong ferromagnetism of the Heusler manganese alloys with As, Sb, Bi, and B.

2. Heusler, on the other hand, has advanced a hypothesis which perfectly explains all the phenomena; for he has not only discovered the ferromagnetic manganese alloys, but he has also first proved, in 1903, that the appearance of the strong ferromagnetism is due to the formation of chemical compounds, and that the ferromagnetism is thus a molecular phenomenon.

3. It is stated and demonstrated in detail which these strongly ferromagnetic chemical compounds are. (Heusler, Haupt, Preusser, Williams, Ross, Hilpert).

The research above referred to proves the Heusler Al-Mn bronze to be, in physical respects, exceedingly interesting material, of valuable properties, especially as regards hysteresis.

4a. By the process described by Heusler the malleable Al-bronzes in particular can be converted into an unmagnetic modification which, suitably aged, yields a strongly magnetic material of very small hysteresis. (Heusler, Asteroth, Take).

4b. By the method of Take the malleable Al-bronzes in particular may, by another ageing process, be transformed into a permanently magnetic modification of exceedingly high intensity.

5. Hypotheses or explaining the strong ferromagnetism of the chemical compounds on the electron theory have been suggested by Richarz, Weiss, and Take.

6. The physical properties mentioned under 4a are due,

according to Richarz, to a very slight formation of complexes of the elementary magnets in the one case, and to a very pronounced formation of such complexes in the other case.

7. According to his experiments the phenomena of ageing are due, according to Take, to two transformations; the first transformation is the gradual formation of the strong ferromagnetic compound of Heusler; the second is the gradual complex formation, as also suggested by Richarz with regard to the experiments by Heusler and Asteroth. This complex formation also gives rise to the enormous coercive forces which are observed in the case 4b.

Prof. A. A. KNOWLTON and Dr. O. C. CLIFFORD (Utah, U.S.A.) also presented a paper on "*The Heusler Alloys.*"

The paper is a contribution to the study of the following questions:—

1. What conditions of preparation and thermal treatment must be observed in order that any alloy of any given composition may be in condition to exhibit the maximum possible intensity of magnetisation at saturation?

2. What are the exact relations between composition and the two factors of magnetic quality—hardness, and intensity of magnetisation at saturation?

3. Upon what factors does the transformation point of a given alloy depend, and what is the exact form of the relation?

The specimens tested were in the form of rings, prepared by prolonged heating in a graphite crucible and cast in a hot carbon mould. A large series of alloys was made, but either on account of poor mechanical or poor magnetic qualities, tests were confined to the following seven:—

| No. | Cu.  | Mn.  | Al.  | History.                                                                                                       |
|-----|------|------|------|----------------------------------------------------------------------------------------------------------------|
| 1.  | 67.8 | 27.8 | 4.4  | Cast from scrap from many previous specimens. Materials have been often cast and re-melted. Chilled from 250°. |
| 3.  | 63.8 | 27.5 | 8.7  | New mixture. Annealed to room temperature.                                                                     |
| 4.  | 63.3 | 26.4 | 10.3 | Cast from scrap. Chilled from dull red heat.                                                                   |
| 5.  | 63.3 | 26.4 | 10.3 | From same melt as No. 4, but annealed to room temperature.                                                     |
| 6.  | 68.0 | 28.0 | 4.0  | New mixture. Annealed to room temperature.                                                                     |
| 7.  | 63.3 | 29.5 | 7.2  | Al added to No. 6, re-melted and chilled from 200°.                                                            |
| 8.  | 60.3 | 25.4 | 14.3 | Al added to No. 7, re-melted and chilled from 250°.                                                            |
| 9.  | 60.2 | 26.7 | 13.1 | Re-melted from scrap. Chilled from 200°.                                                                       |

The results of the tests show that percentage composition is relatively unimportant in determining magnetic quality as compared with heat treatment. Thoroughness of mixing is also an important factor, difficult to separate from heat treatment. It would appear that under the best conditions of mixing and chilling the maximum possible induction, for a given manganese content, increases with increasing percentage of aluminium. Heusler and Starck's assumption that the best results are given by atomic proportions is not regarded as conclusive. For the details of the experiments made the original paper must be consulted, but the authors conclude that it will be impossible to decide what composition will give the alloy of maximum possible magnetisation until the conditions of the best thermal treatment have been worked out over a wide range of composition. Sensitiveness to heat treatment and magnetic hardness are closely dependent upon the proportion of aluminium present, while the transformation temperatures depend largely upon the percentage of copper.

The paper ends with a brief consideration of the following possible hypotheses as to the nature of the magnetic units in the Heusler alloys. These may consist of:—

1. The molecules of a chemical compound of manganese and aluminium, or groups of such molecules.



2. Manganese molecules or groups of such molecules.
3. Complex groups, which form the structural elements of a certain type of mixed crystal, and contain at least two different kinds of chemical molecules.

Prof. PIERRE WEISS (Zurich) communicated a paper entitled "*The Magnetic Properties of the Iron-nickel, Iron-cobalt, and Nickel-cobalt Alloys.*"

When the results of quantitative investigations of magnetic properties are considered from the standpoint of the author's kinetic theory of ferromagnetism, all the metals appear to be homogeneous solid solutions. The saturation intensity of magnetism is the resultant—not the sum—of the molecular moments, and at absolute zero, when heat movements have ceased to exist, the saturation intensity gives the true moment of the molecule. By molecule the author understands the atoms which are rigidly connected with one another; the atoms may also be articulated, *i.e.*, magnetically free to assume any orientation. In the case of substances like oxygen and the salts of metals (in the solid or dissolved states) the coefficient of magnetisation is inversely proportional to the absolute temperature. By multiplying this coefficient by the absolute temperature, we obtain the Curie constant, and the molecular moment (which cannot experimentally be determined in these substances) can be deduced from the Curie constant. When the magnetic moment of the nickel atom is followed through varied temperature conditions in the nickel compounds, the moment is found to be represented by multiples of a common factor, 1123.5, which the author calls the "magneton." At absolute zero the magnetic moment of the Ni-atom is  $3 \times 1123.5$ , or 3 magnetons: at temperatures above the Curie point (at which the strong magnetism disappears) it is 8 magnetons, in salts of 16 magnetons. The same common factor is found in the magnetic moments of the atoms of Co, Mn, Cr, V, Cu, U, and seen therefore to constitute the common elementary magnet.

The assumption of the existence of these magnetons has proved useful in the study of the alloys of iron-nickel, nickel-cobalt, iron-cobalt, which the author has been investigating in conjunction with G. Foëx, F. Hegg, O. Bloch, and A. Preuss. The researches, details of which are given, indicate the existence of the compound  $\text{Fe}_2\text{Ni}$  (30 magnetons, or 10 per atom) already to be traced on the melting-point curve of Guertler and Tammann, though not recognised by them. In solid solutions the molecular magnetic moment is additive, but not in compounds. Conclusions are also drawn as to  $\beta$ -iron (probably  $\text{Fe}_3$ ),  $\gamma$ -iron ( $\text{Fe}_2$ ),  $\delta$  iron (Fe). The interpretation of the results appears clear in the case of the reversible Fe-Ni alloys and of the Ni-Co alloys; the irreversible Fe-Ni alloys and the Fe-Co display complex phenomena. There is, however, also a definite compound,  $\text{Fe}_2\text{Co}$ , which is more magnetic than pure iron, its technical application is being studied. One of the curious features is that nickel, in its reversible ferro alloys, is in a state which the pure metal only assumes at higher temperature; the surrounding iron molecules thus exert a "repercussion" effect upon the interior magnetic condition of the nickel atom. Cobalt does not affect nickel in the same way, but cobalt has this effect in the alloys of cobalt and iron.

The CHAIRMAN communicated a Note in which he criticised the evidence usually brought forward for the existence of a non-magnetic adamantine  $\beta$ -form of iron. There might be modifications in the molecular constitution of iron at high temperatures, but that there was allotropy in the accepted sense of the term remained to be proved. There were iron alloys which were more magnetic than iron, and under the allotropic theory this would mean still another allotropic form of iron. He supported Prof. Knowlton's view that ferromagnetism is neither atomic nor molecular, but crystalline, but more light would have to be thrown on the molecular constitution of iron itself before one could generalise on the question.

Prof. H. DU BOIS opened the general discussion on the papers. He recalled the fact that in addition to the three classical magnetic metals, Weiss has prepared manganese electrolytically which is ferromagnetic. He next referred to the magneto-optical researches that were being carried out in his laboratory, and he stated that a piece of manganese steel which was non-magnetic as a lump distinctly showed the Kerr effect, the effect being variable for different patches on the mirror which reflected the light. This magneto-optical method affords a means of studying the surface patch by patch. A great many other alloys and compounds which are non-magnetic in the lump also show the same effect.

Prof. B. HOPKINSON thought that the most promising direction in which to pursue a systematic study of magnetic materials with a view of throwing light on the nature of magnetism was investigation in fields of very high density. Another promising line of investigation was the relation between the saturation value of magnetisation determined in that way and the temperature effect. As far as was known at present the general character of that relation was much the same as that obtaining between the pressure and temperature of a gas or liquid near its critical-point, and this was a very illuminating analogy. Experiments in high fields were of value in that accidental effects of structure were eliminated. He had shown, for example, that iron could be stretched far beyond the elastic limit in a very powerful field without changing the intensity of magnetisation by so much as 1 per cent.

Dr. W. ROSENHAIN criticised Prof. Hopkinson's statement regarding the "accidental" character of minute internal structure. He considered that while the use of fields of high intensity was of value it would obliterate the effect of many things of interest and importance in themselves. It seemed to him that there were circumstances of a purely molecular character, and also of a structural character, and one would have to try to disentangle the two.

As regards the existence of a hard form of  $\beta$ -iron, he objected to the use of the word "adamantine," although he believed in the existence of a distinctly harder form of iron which was stable at high temperatures, and which could be retained by quenching.

As regards the Heusler alloys, his own work, confined to a range of 11 per cent aluminium and 10 per cent manganese, confirmed Dr. Ross's view as to the non-existence of a ternary compound to the cupra-manganese system which explained the magnetic effects of these alloys. The alloys of aluminium alone are strongly magnetic, and consequently the view he took was that the magnetic qualities of the Heusler Alloys were due to the presence in them in solid solution of  $\text{Mn}_3\text{Al}$ . An ingot of this substance would spontaneously disintegrate to a heap of powder, and it was magnetic both in the bar and in the powdery form.

Dr. CECIL H. DESCH, in a written communication, suggested that the "ageing" of the Heusler alloys may be a complex effect caused by the formation of inter-metallic compounds, the equalisation of composition by diffusion, and the union of ultramicroscopic particles of various phases to form physically more stable aggregates. All of these processes may be concerned in modifying the magnetic properties. Further careful investigation of the alloys, made from pure materials, was necessary in a thoroughly well-equipped laboratory and working at high magnifications.

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Action of Alkalis on Chloraloses.—M. Hanriot and André Kling.—Alcoholic ammonia acts similarly on all chloraloses, giving a substance which contains one atom of hydrogen in the place of one atom of chlorine of the original chloralose. To this substance the authors have given the name dichloroparachloralose. When hydrolysed it gives glucose and dichloraldehyde.—*Bull. Soc. Chim. de France*, xi.—xii. No. 6.

## NOTICES OF BOOKS.

*Practical Chemistry for Engineering Students.* By ARTHUR J. HALE, B.Sc. (London). London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1912.

IN the words of the Introductory Note to this book, which is contributed by Prof. R. Meldola, the aim of the author has been to outline a course of practical chemistry of which the "distinctive feature is the teaching of the subject with a bias towards the use of materials familiar in constructive industry." By following distinctive marks in the text and the directions in the preface three different courses of practical work may be arranged from the book; they vary greatly in length and in the material contained in them, and one or other may be chosen according to the time the student has to give to chemistry. Each course is quite complete in itself. The experiments described include the usual preparations, an outline of qualitative analysis, and some quantitative analysis specially suitable for engineering students; this latter part deals with elementary assaying, and the analysis of water and fuels. The quantitative aspect of the science has been made specially prominent throughout the book, and in style and language it is suitable for the use of students of some maturity of mind and outlook.

*Manufacture of Nitro-lignin and Sporting Powder.* By EARLE DURNFORD. London and New York: Whitaker and Co. 1912.

THIS monograph will probably be read by only a very limited circle, and it seems likely that those who are interested in the manufacture of sporting powders would be glad to be provided with rather fuller details than are to be found in it. The author states very clearly the result of his experience, but references to the views of other workers in the same sphere, and to their publications, would have a very real value for the reader. In the first part of the book the preparation of nitro-lignin is discussed. The essential or specially desirable characteristics of the wood pulp to be used in making it are enumerated, and the treatment of the pulp is discussed in outline. Part II. deals with the manufacture of sporting powder, and gives a summary of the methods of preparing the most important types of "bulk powder."

*Organic Chemistry.* By W. H. PERKIN, Ph.D., Sc.D., LL.D., F.R.S., and F. STANLEY KIPPING, Ph.D., Sc.D., F.R.S. New Edition. London and Edinburgh: W. and R. Chambers, Ltd. 1911.

IT is perhaps unnecessary to call attention to this book, the value of which is well known in most technical schools and colleges in this country. The new edition has been considerably enlarged, and as it now stands the book meets all the requirements of students who are preparing for an Honours Degree Examination. At the same time it is entirely suitable for use as a first text-book of organic chemistry, if the author's hints as to excerpts and omissions are followed. Some completely new chapters and sections, for example, on the Grignard reagents, the cycloparaffins, &c., have been added, and the whole book has undergone a thorough revision.

*Cinquantenaire Scientifique de M. Armand Gautier.* ("Scientific Jubilee of M. Armand Gautier").

THIS volume has been published by the Committee appointed towards the end of 1910 to celebrate the scientific jubilee of M. Armand Gautier. The Committee consisted of influential and eminent men of science, and its requests for subscriptions met with such liberal response that it was enabled to present M. Gautier with a medal in commemoration of the event and a bust executed by M. Theunissen. The volume contains an account of the presentation, which was made on November 26, 1911, and reproduces the discourses of M. Haller and others. Representatives were sent by the Académie des Sciences and the Académie de Médecine, and they expressed in the most laudatory terms their admiration of the work of M. Gautier, whose eloquent reply to the felicitations of his *confrères* is also included.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. cliv., No. 15, April 9, 1912.

**Direct Catalytic Hydrogenation of Benzoic Ethers.**—Paul Sabatier and M. Murat.—The hydrogenations which are easily brought about by the catalytic action of nickel are those which occur rapidly and during a wide range of temperature. Thus benzoic acid cannot be hydrogenated, but if the temperature is kept at 180° and a large excess of hydrogen is used, methyl benzoate can be transformed into methyl hexahydrobenzoate,  $C_6H_{11}.CO_2CH_3$ , and ethyl benzoate into the hexahydrobenzoate. Isoamyl benzoate yields at 200–205° isoamyl-hexahydrobenzoate. The saponification of these ethers yields hexahydrobenzoic acid.

*Bulletin de la Société Chimique de France.*

Vol. xi.—xii., No. 5, 1912.

**Utilisation of the Magnetic Field as a Reagent of Constitution.**—Paul Pascal.—The lowering of the specific susceptibility is the same for all the halogens attached to the same central polyvalent atom, and amounts to  $d = 0.2468.N.10^{-7}$ , where N is a whole number. In each homologous series, if the first term is excepted, the number of aliquot parts in the specific susceptibilities decreases as the atomic weight increases. Thus  $Cl = 19 \times 0.2468.10^{-7}$ ,  $Br = 10 \times 0.2468.10^{-7}$ ,  $I = 4 \times 0.2468.10^{-7}$ . Thus magnetic analysis may be said to point to the subdivision of the diamagnetic atom into sub-atoms, which vary in number and nature according to the element under consideration.

**Chemical Determination of Digitalis.**—James Burmann.—In Keller's method of determining digitalis the digitoxine is lost. In order to avoid this loss alcoholic lead acetate may be added; a voluminous precipitate forms, and may be filtered off and the excess of lead removed from the filtrate by means of sulphuretted hydrogen. Ammonia and chloroform are added and the liquid is evaporated, when all the glucosides are deposited.

## MEETINGS FOR THE WEEK.

MONDAY, June 3rd.—Society of Chemical Industry, 8. "Nature of the Process of Oxidation," by H. E. Armstrong and R. T. Colgate. "Some Present-day Aspects of the Metch Industry," by E. G. Clapton.

— Royal Institution, 5. General Meeting.

TUESDAY, 4th.—Royal Institution, 3. "The Formation of the Alphabet," by Prof. W. M. Flinders Petrie, F.R.S.

WEDNESDAY, 5th.—Society of Public Analysts, 8. "Composition of Milk," by H. D. Richmond. "Application of Adsorption to the Detection and Separation of certain Dyes," by A. C. Chapman and A. Siebold. "Estimation of Dirt in Milk," by W. F. Lowe. "New Method for the Detection and Estimation of Small Quantities of Nitrous Acid," by E. H. Miller. "Use of Methyl-ne Blue as an Indicator in Iodometric Titrations," by F. S. Sinnat. "Estimation of Nitric and Nitrous Acids in Acetic Acid Solution—the Stability of Nitric Acid in Acetic Acid Solution," by K. J. P. Orton.

THURSDAY, 6th.—Royal Institution, 3. "X-rays and Matter," by Prof. C. G. Barkla, F.R.S.

— Royal Society, 4.30. (The Croonian Lecture), "The Process of Excitation in Nerve and Muscle," by Keith Lucas.

— Chemical, 8.30. "Absorption Spectra of various Derivatives of Naphthalene in Solution and as Vapours," by J. E. Purvis. "Velocity of the Hydrogen Ion, and a General Dissociation Formula for Acids," by J. Kendall. "Chloroamino-derivatives of Benzylidene Diamides," by F. D. Chattaway and A. E. Swinton. "Refractivity of Sulphur in various Aliphatic Compounds," by T. S. Price and D. F. Twiss. "Conditions of Iso-dynamic Change in the Aliphatic Ketones—1. The Auto-catalytic Reaction between Acetone and Iodine," by H. M. Dawson and F. Powis.

FRIDAY, 7th.—Royal Institution, 9. "Lord Lister," by Sir William Macewen, F.R.S., &c.

SATURDAY, 8th.—Royal Institution, 3. "The Weather and Utilities of Forecasts," by Willis L. Moore.



# THE CHEMICAL NEWS.

VOL. CV., No. 2741.

## PRECIPITATION OF THE COPPER-ARSENIC GROUP AND THE SEPARATION OF ITS DIVISIONS.

By J. I. D. HINDS.

THE analysis of solutions containing quinquivalent arsenic and bivalent tin is much simplified and expedited by the method here outlined. The facts upon which the method is based are mostly well known, though I have added some definite information, especially as to the loss of arsenious chloride on boiling its acid solution, and the solubility of copper chloride in colourless ammonium sulphide. These facts have been confirmed by careful experiments, and are as follows:—

1. For the ready precipitation of quinquivalent arsenic by hydrogen sulphide a hydrochloric acid concentration above 2 normal is required; for the complete precipitation of other members of the group, notably cadmium, antimony, and tin, the acid concentration must be below one-half normal; to hold in solution the metals of succeeding groups the concentration must be above one-eighth normal. These different concentrations are secured first by evaporation and then by proper dilution.

2. The quantity of arsenious ion lost on long boiling with dilute hydrochloric acid is a function of the quantity present, and also a function of the acid concentration, and when a solution normal in HCl is boiled half away the arsenic lost is less than one-thousandth of the quantity present. I have established this fact by many determinations, an account of which will be given in a subsequent paper. The investigation covered solutions varying in concentration from 0.01 N to normal in arsenious ion. The solutions were distilled half away, and the quantity of arsenic in the distillate determined.

3. The sulphides of arsenic, antimony, and stannic tin are easily soluble in colourless ammonium sulphide. Stannous ion is not thus soluble, and its presence is avoided by oxidising it to stannic ion with a few drops of nitric acid during the boiling.

4. Copper sulphide is only slightly soluble in colourless ammonium sulphide, and in this method the quantity dissolved is inconsiderable, though a little polysulphide may be formed because of separation of sulphur or action of ferric ion.

The process is carried out as follows:—To a given quantity of the solution (say, 45 cc.) add one-ninth of its volume (5 cc.) of concentrated hydrochloric acid and a few drops (0.5 cc.) of nitric acid. The laboratory hydrochloric acid is usually about 10 normal, and the solution is thus made about normal. If much acid is already present allowance must be made for it. Transfer the mixture to an Erlenmeyer flask, and boil it half away under the hood. The residual liquid is about 2 normal in HCl, since but little acid is lost on boiling at this concentration. The nitric acid has oxidised stannous to stannic ion, has prevented the separation of metals by reduction, and has probably raised the valence of a portion of the arsenic. Pass a rapid stream of hydrogen sulphide through the hot liquid, heating again to boiling once or twice, and shaking vigorously. The precipitation of arsenic begins quite promptly and proceeds rapidly. When no more precipitate forms (five to ten minutes), add enough water (80 cc.) to make a volume a little more than twice the original (100 cc.). This reduces the HCl concentration below one-half normal. Continue to pass the gas until the liquid is cold and until no more precipitate forms (ten to fifteen minutes), filter, and wash. For a somewhat similar process, except as to

boiling, see Noyes and Bray in *Journ. Am. Chem. Soc.*, xxix., 167; *Proc.*, 21.

Transfer the precipitate to a beaker, cover it with concentrated ammonium hydroxide, pass a rapid stream of hydrogen sulphide for one or two minutes, warm gently, shake well, filter, and wash. The sulphides of arsenic, antimony, and tin dissolve very promptly, carrying with them generally only a trace of copper. Filtrate and residue are treated in the usual way.

The advantages of this method are as follows:—(1) A definite acid concentration is secured; (2) the precipitation of arsenic is certain, prompt, and complete in a few minutes; (3) after dilution the other metals are thrown down with similar ease and certainty; (4) the use of yellow ammonium sulphide is avoided, and the required ammonium sulphide is formed in the solution; (5) the time is much shortened, thirty to forty-five minutes being sufficient for the whole process.

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## THE PREPARATION AND PROPERTIES OF METALLIC CERIUM.\*

By ALCAN HIRSCH.

### Introduction.

IN view of the amount of research on the rare earths, it is remarkable that little has been done on the metals themselves. (C. R. Boehm, "Seltener Erden"; Moissan, "Chimie Minérale," vol. iii., 776; R. J. Meyer, "Bibliographie der Seltener Erden," complete up to and including the year 1905). This is easily understood, however, when one considers the scarcity of pure material to work with, and the difficulty of reducing these very electro-positive elements from their compounds. What metal has been obtained has been, in most cases at least, small in amount and very impure, usually contaminated with the other members of the group. On account of the rarity of the materials to work with, little has been done in a study of the physical and chemical properties of these rare earth metals, and the field of alloys has been almost untouched.

In the present research, cerium, the leading member of the cerium group, was chosen as the rare earth element to be studied. The investigation was undertaken with a two-fold purpose. First, starting from as pure cerium salt as it was possible to obtain, it was desired to prepare the metal in quantities sufficiently large that its physical and chemical properties could be studied, and a large number of alloys could be made. Second, by preparing metal from the unpurified rare earth residues from monazite sand, obtained as a by-product in the incandescent gas-mantle industry, it was hoped that alloys of commercial value could be obtained. In other words, whereas the application of these residues as oxalates or oxides is very limited to-day, their value might possibly be increased materially if a useful metallic or alloyed product be prepared from them.

The writer gratefully acknowledges his indebtedness to Mr. H. S. Miner, chief chemist of the Welsbach Light Company, for his very generous supply of pure rare earth salts and rare earth residues, and to Profs. Burgess and Lenher, of the University of Wisconsin, for the facilities of their laboratories, and their helpful advice and encouragement during the progress of this research. The electrolytic work was done in the laboratories of Applied Electrochemistry, while the analyses and the chemical preparations were made in the Department of Inorganic Chemistry.

This research was begun in December, 1907, and concluded June, 1911. The actual time devoted to this study covered a period of over three years.

\* A Paper presented at the Twentieth General Meeting of the American Electrochemical Society, Toronto, Canada, September, 1911. From the *Journal of Industrial and Engineering Chemistry*, iii., No. 12.

## Historical.

In 1751 Cronstedt ("Sv. Vet. Akad. Hand.," 1751, p. 227) discovered the mineral cerite in a mine of Bastnaës. In 1784 Bergmann and d'Elhyar ("Sv. Vet. Akad. Hand.," 1784, p. 121) confused the rare earth with lime, and published an incorrect analysis of this mineral cerite. In 1794 Gadolin ("Sv. Vet. Akad. Hand.," 1794, p. 137) discovered the rare earths in a heavy black mineral, afterwards called gadolinite.

In 1804 cerium was discovered simultaneously by Klaproth (*Sitz. Akad. Berlin*, 1804, p. 155) in Germany, and by Berzelius and Hisinger in Sweden (*Ann. Chem. Pharm.*, 1804, l., 245). The first investigator named the oxide ochre earth because of its colour, but Berzelius and Hisinger called the new element cerium, after the planet Ceres. About the same time Vauquelin (*Ann. Chem. Pharm.*, 1804, l., 140) confirmed the discovery of a new earth by analysing cerite, and then undertook the study of the salts of cerium (*Ibid.*, 1805, liv., 28). In 1814 Berzelius and Galin (*Afth. Fys. Kem. Min.*, 1814, iv., 217) separated the oxides of cerium and yttrium. Between this period and that of the famous researches of Mosander, numerous articles were published on cerium and the minerals in which it was found, but the material used was necessarily very impure, and what was called at that time cerium oxide was in reality the mixed oxides of the cerium group.

In 1839 Mosander (*Ann. Chem. Pharm.*, 1844, [3], xi., 464; *Liebig's Ann.*, 1842, xlv., 125) announced that cerium oxide was a mixture of two oxides, those of cerium and lanthanum. In 1841 he stated that cerium oxide contained still another oxide, that of didymium. In 1868 Wolf (*Am. Journ. Sci.*, 1868, [2], xlv., 53) determined the equivalence of cerium, and announced that the so-called cerium compounds were mixtures of two or more rare earth elements. In 1879 Lecoq de Boisbaudran (*Comptes Rendus*, 1879, lxxxix., 212), while examining the didymia obtained from the mineral samarskite, isolated a new element which he called samarium. In 1885 Auer von Welsbach (*Monatsh. Chem.*, 1885, vi., 477) showed that didymia was a mixture of the oxides of two new rare earth elements, neodymium and praseodymium.

At the present time there are about fifteen well identified elements which, for chemical reasons, among other properties that of the insolubility of their oxalates in slightly acid solution, are classified as rare earths. These rare earths are usually sub-divided into three groups in the order of their basicity—the cerium group, the gadolinium group, and the yttrium group. There is no absolute differentiation of one group from another, but rather a gradual transition. Usually only the five elements—cerium, lanthanum, neodymium, praseodymium, and samarium—are included in the cerium group.

The present research is concerned with the cerium group, and principally with cerium itself. But in the rare earths relations between members of the same group are much closer than among other kindred elements, as the platinum metals. For example, the atomic weights of lanthanum, cerium, and praseodymium are, respectively, 139, 140.25, and 140.6; therefore the chemistry of one element concerns that of the other members of the group—to a certain degree at least.

## Previous Work on the Rare Earth Metals.

Two general methods of preparation have been used for the production of the rare earth metals.

1. Reduction of the oxide or chloride by one of the very electro-positive metals.
2. Electrolysis of a fused salt.

Mosander and Marignac (*Ann. Chem. Pharm.*, 1849, [3], xxvii., 209) appear to have been the first to produce metallic cerium by a thermal reduction using the alkali metals. Wöhler (*Liebig's Ann.*, 1867, cxliv., 251) describes the difficulty of the reduction using sodium metal and cerium chloride, and states that 12 grms. of sodium yielded

only 50 to 60 mgrms. of cerium metal. Winckler (*Ber.*, 1891, xxiv., 873) used metallic magnesium and cerium dioxide, and obtained a pyrophoric mixture. Recently some attempts have been made to produce the metals by improved methods of thermal reduction. Matignon (*Comptes Rendus*, cxxxi., 837) used metallic aluminium and magnesium, and Schiffer ("Versuche zur Reduktion d. Cerit-oxygen mit Al; Dissertation Tech. Hochschule," München), in Muthmann's laboratory, experimented with the reduction of the oxides by aluminium. From the writer's own experiences in the attempted thermal reduction of these oxides, which is described further on in this article, it appears that the reduction yields either a lower oxide, an impure mixture of partially reduced metal and oxide, or an alloy of the reduced metal and rare metal, such as an aluminium-cerium alloy.

In 1874 Frey (*Liebig's Ann.*, 1874, clxxxiii., 367) published a notice of the preparation of the rare earth metals in the laboratory of Dr. Schuchardt, in Gortitz, using the electrolytic method of Bunsen. The following year Hillebrand and Norton (*Pogg. Ann.*, 1875, clvi., 466) published an account of their work on the electrolysis of the fused chlorides of cerium and potassium. They succeeded in producing about 6 grms. of cerium. In 1895 Pettersson (*Ber.*, 1895, xxviii., 2419) attempted to electrolyse the oxides, but produced only the carbides. In 1902 Muthmann and his associates (Muthmann, Hofer, and Weiss, *Liebig's Ann.*, 1902, cccxx., 231) published the first of a very comprehensive series of articles on the metals of the cerium group (Muthmann and Weiss, *Liebig's Ann.*, 1904, cccxxi., 1; Muthmann and Beck, *Ibid.*, 1904, cccxxii., 46; Muthmann, Weiss, and Scheidmandel, *Ibid.*, 1907, ccclv., 116). Besides preparing the metals of the cerium group, they devised a new type of electrolytic vessel which they found useful in their method of electrolysis. They have also prepared an alloy which they call "mischmetall," which is an alloy of the cerium-yttrium group metals. Borchers and Stockem (*Journ. Soc. Chem. Ind.*, Abstract, 1907, p. 158) have devised a method in which they use the double cerium-calcium chlorides, and have patented this process (German Patent 172,529). The above mentioned electrolytic methods will be referred to again further on in this article.

## Preparation of Material.

The general scheme followed in this research was to use the mixed rare earth oxides for experimenting on the exact conditions required for the preparation of the desired salt, and, after the proper conditions of the process had been determined, to prepare the pure cerium salt. Oxalates of the rare earths, a by-product of the commercial extraction of thorium and cerium from monazite sand, were employed for these experiments. The oxides, prepared by calcining the oxalates at a temperature of 750–800° C. in a gas muffle furnace, analysed 97.8 per cent rare earth oxides, of which approximately 49 per cent was cerium dioxide. They dissolved completely in nitric acid, and also in hot concentrated hydrochloric acid on digestion, which is usually taken as a check that the cerium content is less than 50 per cent (Moissan, "Chimie Minérale," vol. iii., p. 820).

## Preparation of Anhydrous Chlorides.

The first salts required were the anhydrous chlorides (composition  $\text{RCl}_3$ ). There are several hydrated chlorides of cerium known, of the compositions  $2\text{CeCl}_3 \cdot 15\text{H}_2\text{O}$ ,  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ ,  $\text{CeCl}_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{CeCl}_3 \cdot \text{H}_2\text{O}$ . Cerium chloride is similar to magnesium chloride in that when its solution is evaporated to dryness and calcined,  $\text{HCl}$  is evolved with partial decomposition of the chloride to oxychloride and oxide.

A good many methods have been proposed for the preparation of anhydrous or dehydrated chlorides of cerium, among which may be mentioned the following:—Heat the hydrated chlorides with  $\text{NH}_4\text{Cl}$  until the latter salt is completely volatilised (Matignon, *Comptes Rendus*, 1901,



cxixiii., 239; Muthmann, Hofer, and Weiss, *loc. cit.*). Behringer (*Liebig's Ann.*, 1842, xlii., 134) heated the hydrated chlorides with  $\text{NH}_4\text{Cl}$  in a glass tube in a current of chlorine. Robinson (*Roy. Soc. Proc.*, 1884, xxxvii., 150) heated the oxalates to a temperature of about  $130^\circ$  in dry  $\text{HCl}$  gas until all of the oxalic acid had sublimed, then gradually raised the temperature to a red heat. Didier (*Comptes Rendus*, 1885, ci., 882) heated  $\text{CeO}_2$  in a current of  $\text{CO}_2$  and chlorine. Muthmann and Stutzel (*Ber.*, 1899, xxxii., 3413) passed  $\text{H}_2\text{S}$  over anhydrous sulphate heated to a high temperature, and then a mixture of  $\text{CO}_2$  and dry hydrochloric acid gas. Mosander ("Königl. Sv. Vet. Akad. Hand.," 1826, p. 299) burned cerium in chlorine. Moissan ("Chimie Minérale," vol. iii., p. 827) attacked the carbide by hydrochloric acid gas at  $650^\circ$  or chlorine at  $250^\circ$ . Meyer (Meyer and Wilkins, *Ber.*, 1887, xi., 681) converted the oxides to chlorides by vapours of  $\text{CCl}_4$ .

A number of methods for the preparation of the anhydrous chlorides were tried before a suitable one was found. The large quantity of chloride which was required (several kilograms) necessitated that the preparation should be done in as simple and rapid a manner as was possible. Both aqueous and non-aqueous methods were tried, and below are given the different processes experimented with, and their relative advantages and disadvantages.

One of the best methods for the preparation of this type of chlorides (those that decompose on evaporation and calcination from aqueous solution) is to heat the hydrated chloride with  $\text{NH}_4\text{Cl}$ . In the case of cerium chloride, Muthmann (Muthmann and Weiss, *Liebig's Annalen*, 1904, cccxxi., 1) describes in some detail this method, and mentions the tediousness and care required. To prepare a kilogram, or so may require several days' work to effect the dehydration. The use of a platinum finger crucible is recommended, and not more than 50 grms. of the hydrated cerium-ammonium chloride should be heated at a time. The heating must be done very cautiously, or the product will be contaminated with oxychloride or oxide. The writer has tested thoroughly this method, and finds it very poor in this case for large scale operations. One set of experiments which was tried will illustrate the difficulties encountered. Two kilograms of the mixed oxides were dissolved in 4 litres  $\text{HCl}$  ( $22^\circ \text{Bé.}$ ), and about  $4\frac{1}{2}$  kilograms  $\text{NH}_4\text{Cl}$  were added. Evaporation was carried to dryness in large (35 cm.) porcelain evaporating dishes. About a kilogram of the chlorides was introduced into a large Dixon crucible, which was heated in a gas crucible furnace at a low temperature until the white fumes of  $\text{NH}_4\text{Cl}$  came off copiously. The fumes were conducted out of the window by a suitable flue, and the atmosphere within the furnace was at all times a reducing one. The heating was continued until the contents of the crucible were molten and white fumes ceased to come off. A strong odour of  $\text{HCl}$  gas and chlorine was noticed toward the end of the operation. The product did not melt to a clear liquid as the properly prepared anhydrous chloride does, but fused to a slimy mass. Analysis showed that the chloride was highly contaminated with oxide, and although 1100 grms. were obtained, the product was unsuitable for electrolysis.

Borchers and Stockem (*loc. cit.*) state that many of the difficulties encountered in the dehydration of hydrated cerium chloride can be avoided by the preparation of the double calcium cerium chloride, and that this salt can be prepared in the anhydrous state without decomposition by simple calcination. These results could not be duplicated by the writer. Forty-seven grms. of the hydrated chloride of cerium were dissolved to a clear solution in water slightly acidified with  $\text{HCl}$ , and 15 grms. of  $\text{CaCl}_2$  were added. The solution was evaporated to dryness and calcined. The salt which was obtained did not melt to a clear solution, and was unsuited for electrolysis.

Dennis and Magee (*Am. Chem. Journ.*, 1894, xvi., 649) have prepared the hydrated chloride,  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ , which loses water in a vacuum or over dehydrating agents,

whereas the hydrate,  $2\text{CeCl}_3 \cdot 15\text{H}_2\text{O}$ , does not effloresce when placed over sulphuric acid (Moissan, "Chimie Minérale," vol. iii., p. 827). It was thought that perhaps the anhydrous chloride could be prepared from the hydrated salt,  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ . The concentrated solution of the chlorides, prepared by the action of concentrated  $\text{HCl}$  on the mixed oxides, was cooled to  $0^\circ \text{C.}$  by ice, and dry  $\text{HCl}$  gas was passed into the solution. After a time, crystals began to separate out. They were filtered, dried in the air, and the chlorine content determined by titration with standard  $\text{AgNO}_3$ . The per cent of chlorine was found to be 26.6 per cent, whereas that in  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  is 28.6 per cent. The presence of rare earths other than cerium probably caused the difference in composition. When this salt was heated in a partial vacuum (water-pump) at  $100^\circ$  for two hours, the loss in weight was 4.4 per cent. When dried over  $\text{P}_2\text{O}_5$  in a vacuum desiccator for several days, the loss in weight was about 8 per cent. The salt,  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ , was then dehydrated in dry  $\text{HCl}$  gas. Small quantities of the salt were placed in several porcelain boats in a porcelain tube furnace through which dry  $\text{HCl}$  gas was passed. The maximum temperature in the tube was  $210^\circ$ , and the average temperature was  $195^\circ$ . The product in the boat placed in the centre of the tube lost 35 per cent in weight, and analysis showed a chlorine content of 39.3 per cent. The chlorine content of the anhydrous chloride,  $\text{CeCl}_3$ , is 43.2 per cent. The chloride so prepared melts to a clear liquid. Attempts were then made to prepare the anhydrous chloride on a larger scale by this method; 1500 grms. of the mixed oxides were converted into chlorides, and then the hydrate,  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ , was prepared by the method of Dennis and Magee, described above. The yield of salt was very small, and the operation is a difficult one to perform on a large scale, due to the fact that a low temperature is necessary, and the absorption of  $\text{HCl}$  gas in water is accompanied by a considerable evolution of heat. Moreover, a simple method was found for preparing the monohydrate, and as the dehydration of the septa-hydrate passes through the stage of the monohydrate, this method was abandoned.

As the dehydration of the chlorides appear to be the principal difficulty in the preparation of the anhydrous chlorides, it was thought that a suitable process might be developed by the use of non-aqueous solvents. As the action of non-aqueous solvents was found to be somewhat slower than the action of aqueous ones on cerium compounds, it was desirable that a readily decomposable substance be used as the starting material, and the rare earth carbides were chosen for this reason.

The carbide (see Note),  $\text{RC}_2$ , was prepared by heating the mixed oxides with powdered graphite in an arc furnace. Several kilograms of this material were prepared according to the method of Moissan (*Ann. Chem. Pharm.*, 1896, [7], ix., 302; *Comptes Rendus*, 1896, cxxii., 357). The proper mixture to be heated was found to be 500 parts mixed oxides and 132 parts finest graphite powder. When a graphite crucible was used as one terminal and a graphite rod (about 1 inch diameter) as the other, the carbide was easily prepared on a large scale by using a 25 kw. arc (AC or DC). Care should be taken to protect the eyes properly as the rays emitted from the hot mass are especially harmful as they contain a certain amount of ultra-violet rays.

(NOTE.—Moissan (*Comptes Rendus*, cxxiv., 1233) states that pure  $\text{CeO}_2$  (free from iron and other earths) may be prepared from cerium carbide by fractional treatment of the carbides with dilute  $\text{HNO}_3$ . A modification of this method for the preparation of cerium dioxide free from the other rare earths was made as follows:—100 grms. of the mixed rare earth carbides were ground to a fine powder, and were treated with a small amount of dilute  $\text{HNO}_3$ . After the second treatment iron could not be detected in the residue by the sulphocyanide test. A larger amount of dilute  $\text{HNO}_3$  was added, and the solution after filtration was treated by Mosander's method. (Chlorine passed into the solution which had been made alkaline with  $\text{KOH}$ ).

The precipitate after washing showed only a very faint absorption spectrum. For rapid preparation of cerium dioxide this method appears to be very good. The oxide prepared by this means is yellow when calcined at 100°, but turns darker when heated to 1000°.

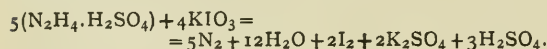
Alcoholic HCl, made by passing dry HCl gas into cooled absolute alcohol, acts readily on the carbides. (Meyer and Keiss, *Ber.*, xxxv., 2622, have used alcoholic HCl for the preparation of cerium salts; they found that this solvent has no action on the oxides, but reacts readily with the carbonates; they did not use the carbide). The solution of the chlorides prepared by this method always contains more or less graphite, and is very difficult to filter because of its viscosity. By evaporation to dryness, the anhydrous chlorides are obtained, but care must be taken to prevent absorption of moisture, as the syrupy liquid is extremely hygroscopic. Several minor difficulties are encountered in this method, the principal ones being the solubility of acetylene in absolute alcohol (six times as soluble as in water), and the lesser solubility of the chlorides in absolute alcohol (one-third as soluble as in water). Because of the above disadvantages, and the expense involved in the use of absolute alcohol and its subsequent loss on evaporation, this method was not suitable to large scale operations. The action of HCl gas and chlorine on the carbides gives chlorides which are highly contaminated with carbon, and are therefore useless for electrolytic purposes, as carbon in a finely divided state with the chlorides will form carbides on electrolysis.

(To be continued)

#### A VOLUMETRIC METHOD FOR THE DETERMINATION OF HYDRAZINE.

By GEORGE S. JAMIESON.

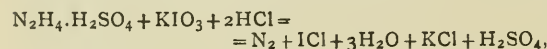
A METHOD for the determination of hydrazine has been described by Rimini (*Gazz. Chim. Ital.*, 1899, xxix., 1., 265) and recently tested further by Hale and Redfield (*Journ. Am. Chem. Soc.*, 1911, xxxiii., 1362). This is based upon the oxidation of the hydrazine compound in aqueous solution by the addition of an excess of standard potassium iodate solution, according to the following equation—



The liquid is then boiled until the iodine is expelled, and the excess of potassium iodate is found after cooling by adding potassium iodide, acidifying with sulphuric acid, and titrating with sodium thiosulphate solution. The chief objection to this method, according to Hale and Redfield, is the length of time required for the analysis.

The method to be described here is based upon the titration of hydrazine by potassium iodate in a strong hydrochloric acid solution, according to the general method of L. W. Andrews (*Journ. Am. Chem. Soc.*, 1903, xxv., 756). It has the advantages of being rapid, and requiring the use of only a single very stable volumetric solution. Besides, as will be seen from the results that follow, it is very accurate.

In order to test the method, a solution containing 3.567 grms. of  $\text{KIO}_3$  in 1000 cc. was prepared. According to the equation of the expected reaction—



the equivalent of this solution is 1 cc. = 0.002169 gm.  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$  and 1 cc. = 0.000534 gm.  $\text{N}_2\text{H}_4$ . Weighed portions of pure hydrazine sulphate were placed in a 250 cc. glass stoppered bottle, together with 20 cc. of water, 30 cc. of hydrochloric acid, and 6 cc. of chloroform.

Then the potassium iodate solution was run in gradually, with shaking between the additions, until the chloroform, after increasing and then diminishing in colour, was just decolorised. The following results were obtained:—

|      | $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$<br>taken.<br>Grm. | $\text{KIO}_3$<br>used.<br>Cc. | $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{SO}_4$<br>found.<br>Grm. | Error.<br>Grm. |
|------|----------------------------------------------------------------------|--------------------------------|----------------------------------------------------------------------|----------------|
| I.   | 0.0487                                                               | 22.5                           | 0.0488                                                               | +0.0001        |
| II.  | 0.0434                                                               | 19.9                           | 0.0432                                                               | -0.0002        |
| III. | 0.0589                                                               | 27.3                           | 0.0592                                                               | +0.0003        |
| IV.  | 0.0472                                                               | 21.9                           | 0.0475                                                               | +0.0003        |
| V.   | 0.0986                                                               | 45.65                          | 0.0990                                                               | +0.0004        |
| VI.  | 0.1060                                                               | 49.00                          | 0.1063                                                               | +0.0003        |

Determinations of hydrazine in the sparingly soluble double sulphates of zinc, cobalt, nickel, and cadmium were made in order to test the method further. The double salts were prepared by mixing hot solutions of the component sulphates in the presence of a little sulphuric acid, and after digesting for some time on the steam-bath, the crystalline products were filtered off by suction, washed with cold water, and dried at 100° C. The titrations were carried out in the same way as described above in the case of the simple sulphate. It was observed that the nickel salt reacted very slowly, apparently on account of difficult solubility, while the other compounds were titrated about as readily as hydrazine sulphate alone.

The following results were obtained:—

|                                                                     | Substance.<br>Grm. | $\text{KIO}_3$<br>used.<br>Cc. | $\text{N}_2\text{H}_4$<br>found.<br>Per cent. | Calcu-<br>lated.<br>Per cent. |
|---------------------------------------------------------------------|--------------------|--------------------------------|-----------------------------------------------|-------------------------------|
| $\text{ZnSO}_4(\text{N}_2\text{H}_4)_2 \cdot \text{H}_2\text{SO}_4$ | 0.1163             | 43.2                           | 19.83                                         | 19.81                         |
|                                                                     | 0.0880             | 32.6                           | 19.77                                         | "                             |
| $\text{CdSO}_4(\text{N}_2\text{H}_4)_2 \cdot \text{H}_2\text{SO}_4$ | 0.1591             | 51.25                          | 17.21                                         | 17.29                         |
|                                                                     | 0.1396             | 45.10                          | 17.25                                         | "                             |
| $\text{NiSO}_4(\text{N}_2\text{H}_4)_2 \cdot \text{H}_2\text{SO}_4$ | 0.0692             | 26.30                          | 20.29                                         | 20.23                         |
|                                                                     | 0.0890             | 33.80                          | 20.28                                         | "                             |
| $\text{CoSO}_4(\text{N}_2\text{H}_4)_2 \cdot \text{H}_2\text{SO}_4$ | 0.1308             | 49.20                          | 20.09                                         | 20.20                         |
| "                                                                   | 0.1059             | 39.70                          | 20.02                                         | "                             |

—*American Journal of Science*, xxxiii., No. 196.

#### THE ISOLATION OF CREATININE FROM SOILS.\*

By EDMUND C. SHOREY.

(Concluded from p. 258).

THE formation of free creatinine from creatinine zinc chloride by boiling with lead hydroxide in the manner already described, the crystallisation of the creatinine so obtained, and observations regarding its crystalline appearance, solubility, and colour reactions may be resorted to in further confirmation of the identity of the compound. The crystalline appearance of creatinine, monoclinic plates or prisms, is, however, not characteristic enough to form the basis of identification.

At this point the question naturally arises whether the isolation of creatinine by the methods described indicates or proves the presence of creatinine in the soil. In deciding this question in the case of other organic compounds isolated from soil the conclusion that the compounds in question must be in the soil as such was based on the fact that all the knowledge of the behaviour of the compounds and their antecedents indicated that they could not be formed by any of the treatments to which the soil or soil extracts had been subjected. In the case of creatinine the question is complicated; first, by the fact that nothing is definitely known regarding its antecedents, *i.e.*, what complex molecule, if any, it is derived from; and, second, by the fact already mentioned that creatinine is readily

\* Published by permission of the U.S. Secretary of Agriculture. From the *Journal of the American Chemical Society*, xxiv., No. 1.



changed to creatine and *vice versa* according to the conditions imposed. Consequently, from general considerations only, it might seem that the creatinine isolated by methods which involve chemical reagents and heat might be derived from creatine or some unknown more complex compound from which creatinine was easily split off. More detailed consideration, however, of the methods involved effectually disposes of the possibility that the creatinine is wholly derived from creatine. While the transformation of creatine and creatinine back and forth into each other is comparatively easy, Folin has shown that it is not so easy as many investigators have assumed ("The Chemistry and Biochemistry of Creatine and Creatinine," Festkrift, Olof Hammersten, III.). All the operations in the methods used, except the final concentration, were such as would result in the change of creatinine back to creatine rather than otherwise. The alkaline extraction and boiling with Fehling's solution would no doubt bring about this change to some extent, so that the creatinine finally obtained was that which had resisted this treatment. The final concentration of the aqueous solution at a low temperature might form some creatinine from creatine, but investigation has shown that this change could be but slight and could never involve the whole of the creatine if it were present. Treatment of these solutions by boiling for several hours with acid resulted in but slightly increased colorimetric readings for creatinine. In other words, the small quantity of creatine present shown by this method was out of all proportion to what would remain after evaporation under reduced pressure, if creatine only had been present in the original solution.

The question of the possibility of the creatinine obtained being formed during the treatment from some more complex antecedent easily broken down, unfortunately can not be disposed of until some definite information regarding such a complex, if there is one, is available.

In the light of all the knowledge available, and on consideration of the bearing of the methods on the final product, it seems safe to conclude that a considerable portion at least and probably all of the creatinine isolated from soils is present in the soils as such.

The possible relation of creatinine to more complex compounds found in the soil or added to soil in dead vegetation is still obscure, but a few observations made in this connection are worthy of record. Nucleic acids of unknown constitution have been found in several soils. (The results of the investigation on nucleic acids in soils will be reported later). Both nucleic acid from soil and yeast nucleic acid prepared by Merck have been found to give the colour reactions for creatinine after heating or even warming for a few minutes with dilute hydrochloric acid. From a solution of yeast nucleic acid treated in this way crystalline creatinine zinc chloride was prepared. It was found, however, that on washing the nucleic acid with cold dilute hydrochloric acid the nucleic acid no longer had the property of giving creatinine on heating with acid. The hydrochloric acid washings, however, after heating showed the creatinine reactions. Whether the explanation of this lies in the inclusion of some creatine in the nucleic acid or whether creatinine is actually split off from the nucleic acid or some complex included with it is as yet unknown. Phytine, or hydroxymethylene diphosphoric acid anhydride, is an organic compound that occurs in the seeds of many plants, and must find its way into the soil. So far this compound has not been isolated from any soil, but it was found that a crude preparation prepared from wheat bran gave on heating with hydrochloric acid a solution which gave the colour reactions of creatinine, and from this solution crystals of creatinine zinc chloride were prepared. On purifying the phytine, however, in the usual way by precipitating it several times as the barium salt it likewise no longer had this property (Patten and Hart, *Am. Chem. Journ.*, 1904, xxxi., 564).

The relation of the creatinine to plants and plant products generally has been already treated in papers from the Bureau of Soils Laboratory (Sullivan, *Journ. Am.*

*Chem. Soc.*, 1911, xxxiii., 2035; and Skinner, *Bot. Gaz.*, 1911), and the only further observations that will be made here bearing on the relation of creatinine to soil organic matter have to do with that added in agricultural practice, viz., organic manures. Creatinine has been found both in stable manure and in fresh cowpea vines as used in green manuring. A sample of well rotted stable manure was extracted with water, and the solution allowed to stand until further fermentation had ceased. From this extract creatinine was isolated by precipitation with Fehling's solution in the same manner as from soil extracts. The resulting solution gave the colour reactions for creatinine, and crystals of both creatinine zinc chloride and creatinine were prepared from the material isolated. Green cowpea vines were crushed and extracted with cold alcohol, the alcohol evaporated at a low temperature, and water added to keep the volume constant, and the solution filtered from insoluble matter. From this solution creatinine zinc chloride was prepared by precipitating the creatinine with Fehling's solution and subsequent treatment with zinc chloride, and also by treating the concentrated aqueous solution directly with zinc chloride.

The work so far done on the quantitative determination of creatinine in soils is but preliminary, and no definite statement regarding the quantity present in soils can be made other than that it is small and apparently but a small portion of the total organic matter. The following facts bearing on this question were established. It is much more easily extracted from soil by alcohol than by water. Usually enough could be obtained by extracting 100 grms. of soil with alcohol to establish its identity, but to accomplish this by aqueous extraction several pounds of soil were usually necessary. In spite of this fact, alcohol extraction does not offer an available method for quantitative determination, as is shown by the following experiment:—One hundred grms. of soil were extracted with alcohol until the concentrated extract no longer gave any reaction for creatinine. Ten mgrms. of creatinine were then added and the soil extracted with alcohol again, and the creatinine determined colorimetrically in the extract obtained. After fourteen hours of continuous extraction only three-tenths of a mgrm. of creatinine was found in solution, and a second extraction of seven hours gave an amount too small to be determined. The colour obtained was not greater after heating these extracts with acid, showing that the creatinine had not been extracted and changed to creatine. Since both water and alcohol extraction seemed unavailable as the basis of a method, attention was given to alkaline extraction. In attempting to carry this out quantitatively several difficulties are met. The complete extraction of the organic matter from soil with dilute alkali is slow and results in a very large volume of solution. Again, this solution is darkly coloured, and the use of a colorimetric method is out of the question unless there is removal of the colour and concentration of the solution. It is possible that alkaline extraction and precipitation of the creatinine from the solution with Fehling's solution or in some other way will ultimately afford a means of determining this compound in soils, but so far these attempts have not given satisfactory figures.

The quantity of creatinine that has been found in soils by any of the methods tried, while small, and representing but a small portion of the organic matter, is by no means negligible, being usually several parts per million of soil and usually equal to and sometimes in excess of the quantity of nitrates normally present.

There is every indication that in no case was there complete extraction of the creatinine, and it is, moreover, possible that this organic soil constituent is a fluctuating quantity, being generated by bacterial or other biological agencies in the soil under certain conditions, and being changed or removed from the soil by growing plants under other conditions.

The initial work on the isolation of creatinine from soil was done with a sample of Volusia silt loam from New York. The sample was from a field that had been in

cultivation for many years. At the time the sample was taken, and for several years previous, the crops on the field had been very poor. So far as could be ascertained the field had never had any application of either commercial fertiliser or stable manure.

After the identity of the compound isolated from the Volusia silt loam was established as creatinine a number of other samples of soil were examined for the presence of this compound. Comparatively few soils have been examined, but so far no soil has been found in which the presence of creatinine was not indicated by the colour reactions given by the extract.

Creatinine zinc chloride in addition to colour reactions was obtained from samples of the following soils:—

Franktown stony loam from Pennsylvania. This sample was taken from a field that had been in cultivation thirty years, but had recently lain idle for three years. When put in cultivation again the crops were still very poor.

Clarksville silt loam from Kentucky. This sample was from an area where the crop yields were fair and the soil responded well to applications of stable manure.

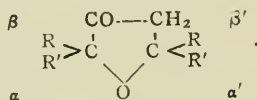
Dunkirk Clay from New York. Fair crop yields had been obtained on the field where the sample was taken.

It would seem, then, that creatinine is probably a normal and constantly occurring constituent of soils. While the soils examined have all been under cultivation some years there is no theoretical reason for concluding that virgin soils differ from cultivated ones in this respect except perhaps in quantity.

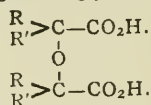
## OXIDATION OF KETOHYDROFURANES.

By G. DUPONT.

By oxidation with potassium permanganate the ketonic chain is opened.



If the carbon substituted near the ketonic group is tertiary, the break occurs in the position  $\beta\beta'$  with the production of a homologue of diglycolic acid,—



If tetramethylketofurane is used we get tetramethyldiglycolic acid, and with dimethyldiethylketofurane we get dimethyldiethyldiglycolic acid.

If the carbon substituted near the ketonic group is not tertiary, the break occurs in the position  $\alpha\beta$  with the production of aceto- $\beta$ -oxybutyric acid from dimethylketohydrofurane.—*Revue Scientifique*, April 27, 1912.

**Determination of Tannin in Wines.**—Philippe Malvezin.—The author has slightly modified his method of determining tannin in wines, and now proceeds as follows:—Ten cc. of an ammoniacal solution of zinc acetate (10 grms. ZnO, 80 cc. of ammonia, and the necessary quantity of acetic acid) are boiled for five minutes with 10 cc. of the wine. The precipitate is filtered off, washed with water, and then with dilute sulphuric acid which dissolves it. The filtrate is titrated with N/10  $\text{KMnO}_4$ , which is added five drops at a time, until a pink coloration is obtained which lasts three minutes. Then  $n \times 0.120 =$  tannin in grm. of gallotannin per litre,  $n$  being the number of cc. of N/10  $\text{KMnO}_4$  used.—*Bull. Soc. Chim. de France*, xi.—xii., No. 6.

## PROCEEDINGS OF SOCIETIES.

### CHEMICAL SOCIETY.

Ordinary Meeting, May 16th, 1912.

Dr. M. O. FORSTER, F.R.S., Vice-President, in the Chair.

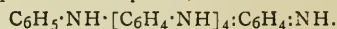
CERTIFICATES were read for the first time in favour of Messrs. Arthur Fred Campbell, M.Sc., Westwood, Middleton, Manchester; Leslie Melville Clark, 3, Harley Road, Hampstead, N.W.; Bhupati Nath Das, M.A., B.Sc., Wari, Dacca, Eastern Bengal; Gerard Irvine Davys, Capt. I.M.S., B.A., M.D., B.Ch., Beechview, Kidbrook Grove, Blackheath, S.E.; Donald M. Ferguson, c/o Acadia Sugar Refining Co., Ltd., Halifax, Nova Scotia; Harold Hartley, M.Sc., Fernbank, Little Switzerland, Douglas, I. of M.; Henry Medley Hatherly, 14, Stackpool Road, Southville, Bristol; Max Henius, Ph.D., 1135, Fullerton Avenue, Chicago, Ill., U.S.A.; Edward Lewis James, Holly Lodge, Larkhall Rise, Clapham, S.W.; William Jewell, 44, Highfield Road, Dartford, Kent; Frederick James Meister, 1, Stanley Terrace, Alva; Robert Charles Menzies, 27, Cluny Drive, Edinburgh; Sidney Morgan, Rubber Growers' Association Laboratory, Pataing, Kuala Lumpur, F.M. States; George Ernest Pearson, Prospect Cottage, Sutton, near Hounslow; William Daveridge Hamilton Shaw, B.Sc., c/o Coppée Coke Oven Co., Ltd., King's House, Kingsway, W.C.; William Thévenaz, D. és Sc., 48, Grey Street, Hull; William Leonard Thomas, 10, Victor Road, Bradford.

Certificates have been authorised by the Council for presentation to ballot under By-Law I. (3) in favour of Messrs. Chatindra Mohan Dutta, M.A., Dacca College, Dacca, India; Anakul Chandra Sircar, M.A., Dacca College, Dacca, India.

Of the following papers those marked \* were read:—

\*116. "Aniline-black and Allied Compounds." Part II. By ARTHUR GEORGE GREEN and ARTHUR EDMUND WOODHEAD.

Willstätter and Cramer (*Ber.*, 1911, xlv., 2162) have advanced the view that the product of reduction of emeraldine or nigraniline with titanium trichloride or phenylhydrazine in the cold is not as the authors have stated leucoemeraldine,  $\text{C}_6\text{H}_5\cdot\text{NH}\cdot[\text{C}_6\text{H}_4\cdot\text{NH}]_4\cdot\text{C}_6\text{H}_4\cdot\text{NH}_2$ , but the mono-quinonoid compound,



Such a view is improbable in face of the fact that the base is practically colourless, but in order to remove all doubt the compound has been subjected to the action of boiling titanium trichloride in an atmosphere of carbon dioxide. The compound remained unaltered, and only a slight change in the titre of the titanium trichloride (due to air oxidation) occurred.

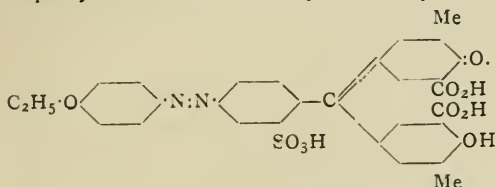
It must therefore be concluded that the base is actually the leuco-compound, and does not contain a quinonoid group. The true mono-quinonoid compound (proto-emeraldine) was prepared by reduction of emeraldine with sulphurous acid. It is a violet base forming yellowish green salts, and dissolves in 80 per cent acetic acid with a grass-green colour. These observations confirm the previous conclusions of the authors as to the number of quinonoid groups in the primary oxidation products of aniline. The "aniline-blacks" of Willstätter and Dorogi are mixtures of these primary products with polymerised derivatives, due to the action of the mineral acid used in purification, and cannot be regarded as identical with the true aniline-black formed on the fibre.

\*117. "Azo-dyestuffs of the Triphenylmethane Group." By ARTHUR GEORGE GREEN and RAJENDRA NATH SEN.

With the object of ascertaining the effect on the colour exerted by two chromophors, the azo-group and the carbinol group present in the para-position with respect to each



other, the authors have prepared a series of azotriphenylmethane and azotriphenylcarbinol dye-stuffs, by condensing azoaldehydes, such as phenetoleazobenzaldehydesulphonic acid,  $\text{OEt}\cdot\text{C}_6\text{H}_4\cdot\text{N}_2\cdot\text{C}_6\text{H}_3(\text{SO}_3\text{H})\cdot\text{CHO}$ , with 2-hydroxytoluic and salicylic acids. The condensation occurs readily in cold concentrated sulphuric acid solution, giving azotriphenyl methane derivatives, which by reason of the presence of the azo-group are yellow dye-stuffs. On oxidation with nitrosyl sulphate they are converted into azotriphenylcarbinols, as, for example, the compound—



The latter are well defined polygenetic dye-stuffs, dyeing wool directly in red shades, and producing various colours with different metallic mordants. The chromium lakes, which are black, can also be produced on the wool fibre by dyeing with the azotriphenylmethane dye-stuffs, and then boiling the wool with an acidified solution of sodium dichromate, when both oxidation and combination with chromium occur together, and the colour changes from yellow through maroon to black.

The conclusion is drawn that the colour of these dye-stuffs is an additive effect produced by the two chromophors acting separately.

\*118. "Investigations on the Dependence of Rotatory Power on Chemical Constitution. Part III. The Rotatory Powers of *ac-Tetrahydro-2-Naphthol* and some of its Esters." By ROBERT HOWSON PICKARD and JOSEPH KENYON.

*ac-Tetrahydro-2-naphthol* has been resolved into its optically active components by the fractional crystallisation from acetone of the *brucine* and *cinchonidine* salts of the *hydrogen phthalic ester*. The active alcohols have a considerably higher rotatory power ( $[\alpha]_D^{20} \pm 67.2^\circ$  in 5 per cent chloroform solution) than that previously given (Pickard and Littlebury, *Trans.*, 1906, lxxxix., 1254), and crystallise very readily from light petroleum in long needles which melt at  $50^\circ$ .

A series of esters of the active alcohols with normal fatty acids (acetic to lauric) has been prepared. The values of the molecular rotatory powers of these gradually diminish from the propionate until the nonoate term is reached, after which the value increases. In close agreement with these results are the determinations of the effect of temperature on the rotatory power of these esters. The acetate with  $[\text{M}]_D^{20} 109.2^\circ$ , propionate with  $[\text{M}]_D^{20} 116.2^\circ$ , *n-valerate* with  $[\text{M}]_D^{20} 113.7^\circ$ , *n-heptate* with  $[\text{M}]_D^{20} 111.5^\circ$ , and the *n-nonoate* with  $[\text{M}]_D^{20} 102.0^\circ$  were obtained as viscous oils at the ordinary temperature, whilst the *laurate* with  $[\text{M}]_D^{20} 107.9^\circ$  solidifies to a crystalline mass and melts at  $36^\circ$ .

#### DISCUSSION.

Dr. A. E. DUNSTAN pointed out that it would be possible, by means of viscosity determinations, to find out whether the mixture of the *d*- and *l*-tetrahydronaphthols was a racemic mixture or a true compound, seeing that the melting-points of the optical antipodes were low enough to enable measurements to be made in the liquid state.

\*119. "Chemical Examination of the Bark of *Euonymus atropurpureus*." By HAROLD ROGERSON.

A description was given of a complete examination of the root-bark of *Euonymus atropurpureus*, Jacquin (Nat. Ord. *Celastraceae*). The new substances which have been isolated and characterised comprise a new crystalline acid, *furan-3-carboxylic acid*,  $\text{C}_5\text{H}_4\text{O}_3$  (m. p.  $121-122^\circ$ ); a new crystalline alcohol designated *euonymol*,  $\text{C}_{21}\text{H}_{30}\text{O}_4$  (m. p.  $248-250^\circ$ ), and a series of new alcoholic substances which give colour reactions similar to the phytosterols, and

have been designated *euonymsterol*,  $\text{C}_{31}\text{H}_{51}\text{O}\cdot\text{OH}$  (m. p.  $137-138^\circ$ ), *homoeuonymsterol*,  $\text{C}_{40}\text{H}_{69}\text{O}\cdot\text{OH}$  (m. p.  $133-134^\circ$ ), and *atropurol*,  $\text{C}_{27}\text{H}_{44}(\text{OH})_2$  (m. p.  $283-285^\circ$ ) respectively.

Various other definite substances have also been isolated and identified, amongst which may be mentioned dulcitol,  $\text{C}_6\text{H}_{14}\text{O}_6$ ; citrullol,  $\text{C}_{22}\text{H}_{36}\text{O}_2(\text{OH})_2$ ; and a mixture of fatty acids. No evidence was obtained of the presence of a glucoside in the bark.

#### DISCUSSION.

Mr. FINNEMORE asked if the substance euonymol obtained in small quantities from the aqueous extract had been tested pharmacologically. Seeing that the drug had been shown by Meyer to contain a heart poison, it seemed to be of some interest, as euonymol appeared to give the same colour reactions as cynotoxin, the heart poison obtained from *Apocynum*.

Mr. ROGERSON, in reply to Mr. Finnmore, stated that euonymol had not been physiologically tested; and in reply to Dr. Harden said that *Euonymus atropurpureus*, Jacquin, was a good source of dulcitol, the yield being equivalent to 2.09 per cent of the weight of root-bark taken.

\*120. "Furan-2:5-dialdehyde." By WILLIAM FRANCIS COOPER and WALTER HAROLD NUTTALL.

In the preparation of dehydromucic acid by the oxidation of *ω*-chloromethylfurfuraldehyde with nitric acid, a considerable quantity of furan-2:5-dialdehyde is produced if the reaction is retarded by cooling. A small quantity of a crystalline acid (m. p.  $196-197^\circ$ ), probably furan-2-aldehyde-5-carboxylic acid (pyromucic aldehyde), is also formed.

*Furan-2:5-dialdehyde* is a white crystalline compound melting at  $109.5-110^\circ$ , which on oxidation gives dehydromucic acid. It is characterised by the blue colour which it gives with thymol and excess of sulphuric acid.

The *diphenylhydrazone* (m. p.  $206-207^\circ$ ), *dioxime* (m. p.  $212.5-213^\circ$ ), *dianilide* (m. p.  $160-161^\circ$ ), and *β-naphthylamine* derivative (m. p. above  $230^\circ$ ) were described.

The dialdehyde is also formed in the retarded oxidation of *ω*-hydroxymethylfurfuraldehyde with nitric acid. *ω*-Hydroxymethylfurfuraldehyde is most conveniently prepared by pouring crude *ω*-chloromethylfurfuraldehyde into a large excess of almost boiling water, without the presence of any reagent capable of reacting with the liberated hydrogen chloride (namely, silver nitrate or barium carbonate) as recommended hitherto.

*β*-Naphthylamine is a very convenient reagent for the identification of aldehydes of the furan series.

The *β-naphthylamine* derivatives of methylfurfuraldehyde (m. p.  $87-88^\circ$ ) and *ω*-hydroxymethylfurfuraldehyde (m. p.  $131-132^\circ$ ) were described.

\*121. "Researches on Santalin. Part I. Santalin and its Derivatives." By JOHN CANNELL CAIN and JOHN LIONEL SIMONSEN.

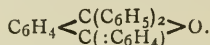
The authors have examined the saplings of *Pterocarpus santalinus* (red sanderswood), and have investigated the colouring matter, santalin, contained in the wood of the tree.

The colourless saplings contain free sugar and a glucoside, which on hydrolysis decomposes into a phlobaphen and dextrose. Santalin, whether obtained from the wood as grown in India, from the rasped wood imported into England, or from the commercial dye-stuff, has the formula  $\text{C}_{15}\text{H}_{14}\text{O}_5$ , and melts at  $226^\circ$ . It forms *diacetyl*, *nitrodiacetyl*, and *dibenzoyl* derivatives, and the *nitro*- and *benzeneazo*-derivatives have been prepared, as well as the *oxime* and *dimethyl ether* and its *nitro*-derivative. Oxidation of the dimethyl ether furnishes veratric and anisic acids, and the nitrodimethyl ether when oxidised yields anisic acid and probably a nitroveratric acid.

\*122. "Action of Grignard Reagents on Esters of Dibasic Acids." (Preliminary Note). By JOHN THEODORE HEWITT and DAVID BERNARD STEINBERG.

By the action of magnesium phenyl bromide on diethyl

phthalate, Shibata (*Trans.*, 1909, xcv., 1449) obtained a compound of the formula  $C_{26}H_{18}O$ , melting at  $194-195^\circ$ , to which he assigned the constitution:—



Certain theoretical conclusions as to the nature of the benzene nucleus were based on the assumption that the compound contained the phenylene group attached to a single carbon atom.

Following Shibata's directions, a compound is obtained identical with diphenylanthrone synthesised by Haller's method from phenyloxanthronyl chloride and benzene in presence of aluminium chloride, as shown by appearance, solubilities, and mixed melting-point,  $193^\circ$ . Shibata's observation that the compound is stable towards bromine and potassium permanganate is thus readily explained.

123. "The Constitution of Aminotyrosine and the Action of Oxidases on some Tyrosine Derivatives." By CASIMIR FUNK.

An attempt has been made to prepare an optically active 3:4-dihydroxyphenylalanine by the action of nitrous acid on aminotyrosine, which was considered to be 3-aminotyrosine. In this way an optically inactive compound was isolated, which possessed the composition of the initial product, but differed from the latter in the colour of the crystals, melting-point, and behaviour towards oxidases.

It was concluded therefore that aminotyrosine is a mixture of 2- and 3-aminotyrosine, the product obtained being 2-aminotyrosine. Further, the action of laccase and tyrosinase on amino- and hydroxy-tyrosine and adrenaline was tested, and it was found that both ferments are able to oxidise these substances.

124. "The Dynamic Isomerism of Ammonium Thiocyanate and Thiocarbamide." By WILLIAM RINGROSE GELSTON ATKINS and EMIL ALPHONSE WERNER.

A careful study of the freezing-points of mixtures of the two isomerides at temperatures above  $130^\circ$  shows a deviation from the simple form of the freezing-point composition diagram given by Findlay (*Trans.*, 1904, lxxiv., 403). Evidence has been obtained indicating the presence in the fusion of the compound  $(CSN_2H_4)_3NH_4SCN$ ; this undergoes dissociation, even below its apparent melting-point ( $144^\circ$ ).

The form of the curve obtained clearly shows that the true melting-point of thiocarbamide itself lies at about  $200^\circ$ ; the very rapid reversion which takes place before this temperature can be reached renders its experimental realisation impracticable. The reversion has also been studied in aqueous and in alcoholic solution; the results obtained in the former case confirm the work of Dutoit and Gagnaux (*Journ. Chim. Phys.*, 1906, iv., 261).

Values were given for the velocity constant of the reversion of ammonium thiocyanate in the liquid phase; the mean value of  $K_1$  is 0.00295, as compared with  $K_1 = 0.00633$  found by Waddell (*Journ. Phys. Chem.*, 1898, ii., 525).

The series of tetrathiocarbamide alkali iodide compounds has been completed by the preparation of the rubidium and caesium derivatives,  $(CSN_2H_4)_4RbI$  (m. p.  $202^\circ$ ) and  $(CSN_2H_4)_4CsI$  (m. p.  $191^\circ$ ).

Lithium and sodium iodides do not form any compounds with thiocarbamide.

The compound  $(CSN_2H_4)_4KI$  has already been described (Werner, *Proc.*, 1906, xxii., 245).

Thiocarbamide and potassium thiocyanate unite to form the compound  $(CSN_2H_4)_3KSCN$  (m. p.  $143^\circ$ ), analogous to the above ammonium compound.

125. "Properties of Mixtures of Allyl Alcohol and Water." (Part I.). By THOMAS ARTHUR WALLACE and WILLIAM RINGROSE GELSTON ATKINS.

In order to be able to analyse accurately the mixtures of the alcohol with water during the subsequent work, a complete density-composition diagram was plotted for  $0^\circ$ . Analysis may also be satisfactorily carried out by a slight

modification of the bromine absorption method. A large contraction in volume was found, amounting to 2.54 per cent with a mixture containing 39 per cent of alcohol when determined at  $0^\circ$ . The pure alcohol had  $D_{20} 0.8629$ , and boiling-point  $96.95^\circ$ . The alcohol and water afford a binary mixture of constant boiling-point, as already known. The composition of this is 72 per cent of alcohol and 28 per cent of water, and its boiling-point is  $88.0^\circ$ . In determinations of the above composition, the middle-point distillation method of S. Young gave values which agreed closely with those obtained from the density curve. The behaviour of the alcohol on distillation with benzene and water is at present under investigation.

126. "A Modification of the Beckmann Apparatus." By EDMUND KNECHT and JOHN PERCY BATEY.

The authors find that by employing a heating coil of suitable resistance, internal electrical heating can be used in the Beckmann apparatus for determining the molecular weight of substances in aqueous solution without electrolysis taking place. Quite constant readings are obtained without any special precautions. The apparatus has been used for determining the molecular weights of certain dyestuffs, such as benzopurpurine and indigo-white.

127. "Alkaline Cupric-compounds." By SPENCER UMFREVILLE PICKERING.

Twenty-four cupri-compounds of tartaric and racemic acids were described, representable by ten general formulæ, derived either from a molecule of the copper salt or of the double salt of copper and the alkali metal, by the copper atom becoming quadrivalent, and the introduction of OH, OM', or  $O_2Cu$  groups through the action of alkali. Four of the salts are represented by the empirical formula  $(R_2CuM')_{3.5}CuO$ ; in the others, which are alkaline in reaction, the ratio of copper to alkali metal is 1:1, 1:2, 1:2.5, 1:3, 1:4, 1:5, and 1:6. All the compounds except those with the ratio 1:1 are crystalline. Copper racemate itself exists in two different forms, one of which is probably a "cupri"-salt, and is much more soluble than the ordinary racemate.

128. "The Constituents of West Indian Satinwood." By SAMUEL JAMES MANSON AULD and SAMUEL SHROWDER PICKLES.

An investigation of West Indian satinwood (*Zanthoxylum flavum*, Vahl.; *Fagara flava*, Kr. et Urb.) has been made, the primary object of which was to determine whether it contained irritating or poisonous principles, such as have already been shown to be present in East Indian satinwood (Auld, *Trans.*, 1909, xcv., 964). The examination has shown it to contain several interesting compounds of a lactic character, together with a number of non-crystalline resins. These include a colourless crystalline compound,  $C_{11}H_{10}O_3$  (m. p.  $124-126^\circ$ ), and a pale yellow crystalline substance,  $C_{14}H_{12}O_3$  (m. p.  $133^\circ$ ). Derivatives of the latter have been obtained, and its general behaviour has been studied. It yields a characteristic dibromide,  $C_{14}H_{12}O_3Br_2$  (m. p.  $125^\circ$ ), in which, on treatment with water, one of the bromine atoms is replaced by a hydroxyl group, giving a compound,  $C_{14}H_{13}O_4Br$  (m. p.  $168-169^\circ$ ). A series of resins has also been separated, as well as a further crystalline compound (m. p.  $112-114^\circ$ ).

The pharmacological action of the various constituents of the wood is at present under investigation by Prof. Cash, of Aberdeen University.

129. "Optically Active Derivatives of l-Methoxy- and d-Dimethoxysuccinic Acids." (Preliminary Note). By CHARLES ROBERT YOUNG.

In continuation of previous work (Purdie and Young, *Trans.*, 1910, xcvi., 1524), d-dimethoxysuccinilanilide and d-dimethoxysuccinilanilic acid have been prepared by the action of aniline on d-dimethoxysuccinic acid and its anhydride respectively. The anilide crystallises from benzene in slender needles (m. p.  $137-139^\circ$ ), and in dilute acetone solution has  $\alpha_D +259^\circ$ . The anilic acid (m. p.  $120-122^\circ$ ) separates from solution in acetone in small

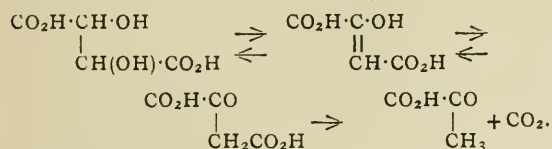


prisms; in the same solvent it has  $n_D^{20} + 13.4$ . Attempts are now being made to prepare, from the anilic acid, the corresponding anil and isoanil. Other active derivatives of *l*-methoxy- and *d*-dimethoxy-succinic acids of these types are under investigation with the view of studying their optical behaviour.

130. "The Mechanism of the Racemisation of some Hydroxy-acids by Heat." By DAN IVOR JAMES and HUMPHREY OWEN JONES.

The process of racemisation of malic acid in aqueous solutions (concentration about 8 per cent) at about  $160^\circ$  has been studied, and it has been found that racemisation takes place through the intermediate formation of fumaric acid, a change which is reversible.

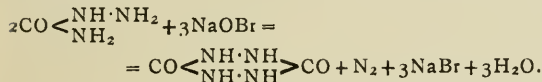
The corresponding change in the case of tartaric acid would produce hydroxyfumaric acid, as suggested by Nef; this acid itself or its isomeride, oxalacetic acid, would be expected to lose carbon dioxide and yield pyruvic acid. The formation of considerable quantities of pyruvic acid has been established, and it is probable that the following changes take place:—



131. "The Action of Sodium Hypobromite on Carbanide Derivatives." By FRANK WILLIAM LINCH.

The author has studied the regulated oxidation of certain carbanide derivatives by means of sodium hypobromite.

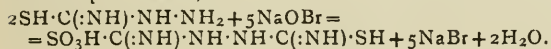
With semicarbazide the main product is *p*-urazine (yield, 80 per cent of the theoretical) when the substances are allowed to react in the proportions indicated by the following equation:—



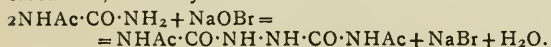
The reaction proceeds in stages, with the intermediate formation of hydrazodicarbonamide.

*p*-Urazine is very sensitive towards oxidising agents, the first product being 3:6-diketo-1:2:3:6-tetrahydro-1:2:4:5-tetrazine,  $\text{CO} < \begin{array}{c} \text{N}=\text{N} \\ \text{NH}\cdot\text{NH} \end{array} > \text{CO}$ .

Thiosemicarbazide and hydrazodicarbonthioamide when oxidised by hypobromite produce hydrazodicarbonthioamidesulphonic acid,—



No condensation product could be obtained from carbamide, but acetylcarbamide condenses as follows:—



The author proposes to extend the investigation to other carbamide derivatives.

132. "Keto-enolic Ethers and Derivatives of Dibenzoylmethane." By ROBERT DUNCOMBE ABELL.

The object of this work was to prepare ethers of the type  $\cdot\text{C}(\text{OR})\cdot\text{CH}\cdot\text{CO}\cdot$  by the silver oxide method, which did not appear to have been applied to the keto-enolic forms of the 1:3-diketones.

Phenyl  $\alpha$ -hydroxystyryl ketone,  $\text{OH}\cdot\text{CPh}\cdot\text{CH}\cdot\text{COPh}$ , reacting with methyl iodide gave *aa*-dibenzoylthane,  $\text{CHBz}_2\cdot\text{CH}_3$ ; and with ethyl iodide gave *a*-dibenzoylpropane,  $\text{CHBz}_2\cdot\text{CH}_2\cdot\text{CH}_3$ , and a small quantity of phenyl  $\alpha$ -ethoxystyryl ketone,  $\text{OEt}\cdot\text{CPh}\cdot\text{CH}\cdot\text{COPh}$ .

The methyl and ethyl esters of phenyl  $\alpha$ -hydroxystyryl ketone were obtained in good yield from phenyl  $\alpha$ -bromostyryl ketone by the action of sodium methoxide and ethoxide respectively.

Further, the sodium derivative of phenyl  $\alpha$ -hydroxystyryl ketone reacts, under suitable conditions, with:—

1. Methyl iodide to give *a*7-dibenzoylthane.
2. Ethyl iodide to form *aa*-dibenzoylpropane (compare Miss Smedley, *Trans.*, 1910, xcvi., 1492).
3. Ethyl iodoacetate to produce ethyl  $\beta$ -dibenzoylpropionate,  $\text{CHBz}_2\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$ .
4. Iodine to give *s*-tribenzoylmethane,  $\text{CHBz}_2\cdot\text{CHBz}_2$ , and dibenzoyliodomethane,  $\text{CHBz}_2\text{I}$ .
5. Benzyl iodide to form *aa*-dibenzoyl- $\beta$ -phenylethane,  $\text{CHBz}_2\cdot\text{CH}_2\cdot\text{Ph}$ .
6. Benzoyl chloride to give the  $\alpha$ - or diketo-enolic form of tribenzoylmethane,  $\text{CBz}_2\cdot\text{CPh}\cdot\text{OH}$ , and not the triketo-form (compare Claisen, *Annalen*, 1896, ccxc., 95; Baeyer and Perkin (*Ber.*, 1883, xvi., 2135; Perkin, *Trans.*, 1885, xlvii., 253).

Dibenzoyliodomethane and *aa*-dibenzoyl- $\beta$ -phenylethane show feeble enolic properties.

133. "Derivatives of Phenyl Styryl Ketone. Part I. The Tautomeric Forms of Dibenzoylmethane." By ROBERT DUNCOMBE ABELL.

This revision of Wislicenus's work (*Annalen*, 1899, cccviii., 219), undertaken after identifying phenyl  $\alpha$ -ethoxystyryl ketone with "dibenzoylmethane," was continued even after the appearance of Ruhemann and Watson's paper (*Trans.*, 1904, lxxxv., 456) as several new results had already been obtained.

Phenyl styryl ketone combines with bromine to form two isomeric dibromides,  $\text{CHPhBr}\cdot\text{CHBr}\cdot\text{COPh}$ , the one melting at  $158^\circ$  (Claisen and Claparède, *Ber.*, 1881, xiv., 2464; Wislicenus, *loc. cit.*), the other in very small yield melting at  $122^\circ$  (Miss Smedley, *Proc.*, 1909, xxv., 259, gives  $113^\circ$ ; and Pond, York, and Moore, *Am. Chem. Journ.*, 1901, xxiii., 789, 108—109).

The dibromide, melting at  $122^\circ$ , can be obtained in 90 per cent yield by the union of hydrogen bromide with phenyl  $\alpha$ -bromostyryl ketone,  $\text{CBrPh}\cdot\text{CH}\cdot\text{COPh}$ , in carbon disulphide solution.

Phenyl  $\alpha$ -bromostyryl ketone was prepared from the dibromide melting at  $158^\circ$  by the action of excess of potassium acetate in alcoholic solution (compare Wislicenus, *loc. cit.*).

According to Wislicenus, equimolecular quantities of phenyl  $\alpha$ -bromostyryl ketone and sodium hydroxide in alcoholic solution when heated for half-an-hour gave a trace of phenyl  $\alpha$ -hydroxystyryl ketone and "dibenzoylmethane," now known to be phenyl  $\alpha$ -ethoxystyryl ketone.

The author finds that under these conditions phenyl styryl ketone is also formed.

If the same quantities of the reacting substances are heated only until the alkaline reaction disappears, phenyl  $\alpha$ -hydroxystyryl ketone is not formed.

Wislicenus's "dibenzoylmethane" is phenyl  $\alpha$ -ethoxystyryl ketone. The "dibenzoylmethane" of Baeyer and Perkin (*Ber.*, 1883, xvi., 2134) and of Claisen (*Ber.*, 1887, xx., 655) is phenyl  $\alpha$ -hydroxystyryl ketone. Dibenzoylmethane,  $\text{C}_6\text{H}_5\cdot\text{CO}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{C}_6\text{H}_5$ , is still unknown.

134. "The Interaction between Di-iodoacetylene and Organic Sodio-derivatives." By HUGH VERNON THOMPSON.

Di-iodoacetylene, although a very unstable substance, resembles the metallic derivatives of acetylene in that it exhibits but little tendency to react with the ordinary organic reagents; it therefore appeared of interest to examine its behaviour toward such highly reactive compounds as sodiomalonic and sodioacetoacetic esters.

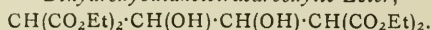
#### Preparation of Di-iodoacetylene.

The method for preparing di-iodoacetylene given by Dehn (*Journ. Am. Chem. Soc.*, 1911, xxxiii., 1598) only yields satisfactory results if certain precautions not mentioned by that author are taken. It is desirable to purify the acetylene obtained by the action of water on commercial calcium carbide, by passing it through an aqueous solution of ammonium persulphate. The sodium hypochlorite solution, which is dropped into the solution of

potassium iodide during the passage of the acetylene gas, should be prepared by passing chlorine into a 10 per cent solution of sodium hydroxide, and care must be taken that no excess of chlorine is ultimately present; if more concentrated sodium hypochlorite solutions are used, or if they contain free chlorine, the formation of di-iodoacetylene is considerably or completely inhibited. The preparation of the di-iodoacetylene should be carried out as rapidly as possible, and the precipitated substance collected immediately, washed, dried on porous earthenware, and dissolved in light petroleum; if left in contact with the mother-liquor the di-iodoacetylene re-dissolves in part, leaving an unstable material, which explodes with violence when separated and left in contact with the air.

When the precautions indicated above are taken, the yield of crude di-iodoacetylene represents 80 to 90 per cent of that theoretically obtainable from the amount of potassium iodide used; after purification by crystallisation from light petroleum, the yield is found to be smaller, because of the presence of a material insoluble in that solvent.

#### Dihydroxybutanetetracarboxylic Ester,



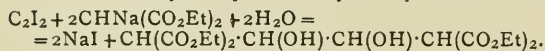
One molecular proportion of di-iodoacetylene is boiled with four molecular proportions of monosodiummalonic ester in alcoholic solution for several hours on the water-bath; the reaction is performed in the dark in order to prevent decomposition of the di-iodoacetylene by light. The alcohol is then distilled off, and the residue, after addition of water, extracted with ether; the ethereal extract on evaporation yields a viscous reddish brown residue, which contains no halogen, and which could not be caused to crystallise. This residue is distilled under ordinary pressure, and then undergoes considerable decomposition; the distillate, however, is a colourless oil, which slowly becomes partly crystalline. The crystalline material after separation and re-crystallisation from ether is obtained in small compact colourless crystals, which melt at  $72^\circ$ :—

0.2062 gave 0.1250  $\text{H}_2\text{O}$  and 0.3835  $\text{CO}_2$ .  $\text{C} = 50.72$ ;  $\text{H} = 6.79$ .

$\text{C}_{16}\text{H}_{20}\text{O}_{10}$  requires  $\text{C} = 50.77$ ;  $\text{H} = 6.93$  per cent.

1.9917 grms. dissolved in 26.45 grms. of glacial acetic acid depressed the freezing-point of the solvent by  $0.81^\circ$ . The molecular weight indicated is thus 363. 1.6347 grms. in 25.68 grms. of the same solvent similarly depressed the freezing-point by  $0.64^\circ$ , indicating a molecular weight of 390. The mean of the two determinations, namely, 376, agrees well with that corresponding with the molecular composition stated, namely, 378.

There seems little doubt that the substance is the dihydroxy butanetetracarboxylic ester which Polonowsky obtained (*Annalen*, 1888, ccxlii., 3) as a yellow syrup by the action of glyoxal and malonic ester in presence of zinc chloride. The formation of this product by the reaction now described may be represented by the equation—



On preserving the oily residue from which the above-described crystalline product had been separated, it gradually crystallised, and the crystalline compound thus obtained, after re-crystallisation from ether, yielded colourless crystals melting at  $47-48^\circ$ . The quantity of material obtained was too small for further examination, but it is probable that the two crystalline substances melting at  $72^\circ$  and at  $47-48^\circ$  are the *cis*- and *trans*-modifications of dihydroxybutanetetracarboxylic ester.

Di-iodoacetylene reacts with sodioacetoacetic ester in alcoholic solution, and after evaporation of the alcohol, treatment of the residue with water, extraction of the aqueous solution with benzene, and evaporation of the benzene, an oily residue was obtained which was obviously a mixture; it could not be caused to crystallise and decomposed when distilled under diminished pressure.

The attempt to cause di-iodoacetylene to condense with

sodium ethoxide under various conditions led in each case to the isolation of a small yield of a dark coloured pungent-smelling liquid corresponding in properties with the ethyl iodo-orthoacetate,  $\text{CH}_3\text{I} \cdot \text{C}(\text{OEt})_3$ , prepared by Nef (*Annalen*, 1897, ccxcviii., 350) in the same way.

This investigation, commenced at the suggestion of Prof. Pope, will be continued.

135. "The Rotatory Powers of the *d*- and *l*-Methylethylphenacylthetine Salts." By CLARA MILLICENT TAYLOR.

Externally compensated methylethylphenacylthetine bromide has been prepared in quantity, and resolved into its optically active components by the aid of the corresponding salts formed with *d*- $\alpha$ -bromocamphor- $\pi$ -sulphonic acid. An extensive series of determinations of the rotation constants for the mercury green, mercury yellow, and sodium yellow lines has been made of the salts of *d*- and *l*-methylethylphenacylthetine with the latter acid, picric acid, and styphnic acid in various solvents.

## NOTICES OF BOOKS.

*An Introduction to the Study of Fuel.* By F. J. BRISLEE, D.Sc. London: Constable and Co., Ltd. 1912.

THIS book is the first of a series of text-books on the outlines of industrial chemistry which are intended to bridge over the gap between the elementary text-book of general chemistry which the student uses in his school days and the treatises which he has to read early in his technical course. This volume may be read easily and profitably by a student who knows, comparatively speaking, only very little chemistry, and he will find that when he takes up larger works he has very little to unlearn. The author has fully recognised the importance of imbuing his readers with a scientific habit of thought and training them to attack problems in the right spirit, and he has treated the "general principles" very successfully. In the special part he describes methods of analysing fuels fully enough to enable the reader to understand thoroughly the processes employed, and he gives many worked examples to explain all kinds of calculations. The most difficult chapter in the book is undoubtedly that on gaseous fuels, and in order to follow it the student would have to have some knowledge of the integral calculus, but on a first reading it might quite well be omitted altogether without damaging the continuity of the text.

*An Experimental Course of Physical Chemistry.* Part II. By JAMES FREDERICK SPENCER, D.Sc. (Liverpool), Ph.D. (Breslau). London: G. Bell and Sons, Ltd. 1911.

IN the second volume of this short experimental course of physical chemistry, dynamical experiments are described. As in the first volume short theoretical discussions of the principles involved in each group of experiments precede the full experimental details. In every case the author describes thoroughly tested methods, and he is careful to give all particulars and precautions necessary to ensure accurate results. Since his experience has shown that the chemical student's knowledge of the methods of physics often needs supplementing, he describes in detail the measurement of electrical quantities. A chapter on radioactivity is included, and some interesting experiments in the subject are described.

*Natural Sources of Energy.* London: British Science Guild.

THIS report has been prepared by a Committee of the British Science Guild appointed to consider the question of the Conservation of Natural Sources of Energy. This Committee, recognising the disastrous results which must



come from the misuse and waste of our chief source of energy—coal—carefully considered the economising of coal supplies, and a long paper by Dr. Beilby gives a summary of the work of the Royal Commission, discusses the conclusions it reached, and suggests that the establishment of a permanent committee might be of practical utility. In another paper the increased use of internal combustion engines is advocated. The papers forming the Report include short discussions by Sir William Ramsay on the possibility of using the energy of radio-active transformations, and by Prof. Strutt on the internal heat of the earth. In both cases it is pointed out that there is no prospect of these sources of energy being converted into work on a large scale. Water-power is also shortly discussed, but wave-power and wind-power, &c., are left for a later Report.

*Official Chemical Appointments.* Fourth Edition. London: The Institute of Chemistry of Great Britain and Ireland. 1912.

This list of official chemical appointments is arranged in three main sections. The first contains a table of the chief appointments in Great Britain and Ireland, and the second a list of the most important professorial and teaching appointments in various parts of the British Empire. The third part gives concise information relating to Societies and Institutes which are interested in the advancement of chemical knowledge. The sciences closely allied to chemistry, such as mineralogy and bacteriology, are included. The list is invaluable for those who are contemplating the adoption of some branch of chemistry as a profession, particularly as it gives short notes on the conditions on which some important appointments are made, and on the qualifications which are required of candidates for them.

*Zur Kenntnis des Negative Druckes in Flüssigkeiten.* ("A Contribution to the Knowledge of Negative Pressure in Liquids"). By JULIUS MEYER. Halle-a-S.: Wilhelm Knapp. 1911. (2.10 M.).

This monograph opens with a short section in which a historical account is given of the results which have been obtained by early workers on the negative pressure of liquids. Some allusion is made to the biological aspects of the problem. The author's own experiments, which he describes in detail, were aimed at perfecting methods of accurately measuring the negative pressure. He explains the construction of an apparatus for the purpose which is convenient and easily manipulated, and by means of which the alteration in the volume of the liquid could be established. With this apparatus he measured the dilatation coefficients of water, absolute ethyl alcohol, &c., and gives in the monograph the experimental details, with the results of his determinations.

## CORRESPONDENCE.

THE LATE DR. EDWARD DIVERS.

To the Editor of the Chemical News.

SIR,—In memory of the late Dr. Edward Divers, M.D., D.Sc., F.R.S., a meeting of his old friends, colleagues, and students was held in one of the University Buildings in Tokyo, on Friday, May 10th, at 4.30 p.m. Prof. Joji Sakurai, D.Sc., LL.D., was in the Chair, and Prof. T. Haga, D.Sc., delivered a Memorial Lecture, in which he dwelt at considerable length on the life and work of his lamented teacher. Dinner was held afterward, and at the table several speeches were made, all paying tribute to the memory of the distinguished English chemist, whose teaching and personality had a very important influence upon the progress of chemistry in Japan.—I am, &c.

JOJI SAKURAI.

Science College, Imperial University,  
Tokyo, Japan, May 14th

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. cliv., No. 16, April 15, 1912.

Oxidation of some Ketohydrofuranes.—Georges Dupont.—Potassium permanganate acts more or less energetically on the ketohydrofuranes. When the substituted carbon in the neighbourhood of the ketonic function is tertiary, a homologue of diglycolic acid is obtained. In the case of dimethylketohydrofurane the product is aceto-8-oxybutyric acid.

Action of Oxyurea on  $\beta$ -Ketonic Ethers.—André Meyer.—When oxyurea acts on acetyl acetic ether at 10° an addition product is formed of formula  $C_7H_{14}O_5N_2 \cdot C_6H_{10}O_3 + CO(NH_2)(NHOH) = C_7H_{14}O_5N_2$ . A second and very similar product can be isolated; it appears to have the formula  $C_7H_{12}O_4N_2 + 0.5H_2O$ . By the action of oxyurea on benzoyl acetic ether,  $C_{12}O_4H_{14}N_2$ , is obtained.—

$C_{11}H_{12}O_3 + CO(NH_2)(NHOH) = C_{12}H_{14}O_4N_2 + H_2O$ , and similarly with oxalacetic ether,  $C_9H_{14}O_6N_2$ , is formed, as well as a small quantity of another product, which is probably a hydrate of the former.

Various Syntheses starting from Butyrene.—M. Amouroux and M. Murat.—Isoamyl magnesium bromide gives with butyrene the tertiary alcohol isoamylidipropylcarbinol. This alcohol is readily dehydrated by means of alumina at 300°, the product being the ethylenic hydrocarbon,  $C_{12}H_{24}$ . Butyrene reacts similarly but less slowly on isobutylmagnesium chloride, giving isobutylidipropylcarbinol, from which the hydrocarbon,  $C_{11}H_{22}$ , may be obtained. With phenyl magnesium bromide the product is phenyl dipropylcarbinol. Similar reactions occur with benzyl magnesium chloride and cyclohexyl magnesium chloride.

No. 17, April 22, 1912.

Syntheses by means of Mixed Organo-metallic Derivatives of Zinc.—E. E. Blaise.—The author has already shown that the chlorides of the  $\alpha$ -acidoxyl acids react with the mixed organo derivatives of zinc to give cycloacetals. By analogy the chlorides of the  $\alpha$ -formoxyl acids should give cycloacetals which would undergo hydrolysis to give aldehydes. The author has proved that this is the case, and has thus obtained butanol, starting from lactic acid or from  $\alpha$ -oxyisobutyric acid. This method constitutes a synthesis of aldehydes by the fixation of any carbon group to the aldehyde group, CHO. The yields, though satisfactory, are not higher than those obtained by other methods.

Dehydration of Pseudobutylidiphenylcarbinol.—M<sup>me</sup>. Ramart-Lucas.—When phenyl magnesium bromide acts on trimethylacetophenone a tertiary alcohol of formula  $C_{17}H_{20}O$  is obtained. On dehydration it gives a hydrocarbon,  $C_{17}H_{18}$ . The oxidation of this hydrocarbon yields acetophenone, benzophenone, carbon dioxide, and an acid,  $C_{17}H_{18}O_2$ , which fuses at 173°. The formation of benzophenone can be explained by supposing that the hydrocarbon contains a trimethylenic chain; i.e., that it is 1.1-dimethyl-2.2-diphenyl-trimethylene,

$$\begin{array}{c} CH_2 \\ | \\ (CH_3)_2 - C = C = (C_6H_5)_2 \end{array}$$
 But to explain the production of acetophenone it may be supposed that the original tertiary alcohol (which is 1.1-diphenyl-2.2-dimethyl-1-propanol) contains a small amount of an isomer in which the group  $CH_3 - C - C_6H_5$  is present.

Action of Hydrogen Peroxide on Bromothiophenes.—Maurice Lanfrey.—Monobromothiophene is decomposed

by hydrogen peroxide, some bromine being set free. This bromine reacts on the rest of the monobromothiophene, giving the dibromo-compound. At the same time some of the monobromo-compound is destroyed, with formation of sulphuric acid. Dibromothiophene is also partially decomposed by  $\text{H}_2\text{O}_2$ , but the action is much less marked than with the monobromo-derivative. Tri- and tetrabromothiophene are unaltered by hydrogen peroxide. Thus the substitution of two or more hydrogen atoms of the thiophene molecule by bromine makes it much more stable.

**Reduction of  $\beta$ -Diketones.**—Edouard Bauer.—The reduction of acetyl acetone by sodium and alcohol leads to the formation of glycol. With benzoylacetone the reduction goes further, and the CO group next to the phenyl radical is reduced to  $\text{CH}_2$ . The reduction of dibenzoylmethane does not give the corresponding glycol, but a later reduction product, one of the ketonic groups being reduced to  $\text{CH}_2$ .

*Bulletin de la Société Chimique de France.*  
Vol. xi.—xii., No. 6, 1912.

**Action of Nitrogen and Oxygen on Magnesium.**—C. Matignon and M. Lassieur.—Nitrogen combines directly with magnesium above  $670^\circ$ , while oxygen begins to act on it at  $600^\circ$ . Between these two temperatures the nitrogen can be isolated from a mixture of nitrogen and oxygen. Above  $670^\circ$  magnesium fixes both elements at very different rates. Magnesium nitrate can be obtained by heating magnesium to a red heat in air; the presence of mercury does not appear to facilitate the combination of magnesium with nitrogen and oxygen.

**Molecular Compounds of Aromatic Amines with Nitro-derivatives.**—D. E. Tsakalotos.—The remarkable orange-red colorations observed when aromatic amines are mixed with nitro-derivatives (nitrobenzene, &c.) are probably due to the formation of molecular compounds, but the fusion curves show that these compounds are completely dissociated in the solid state, and the viscosity and density curves show that they are also dissociated to a very large extent in the liquid state. The only facts which go to prove the existence of these very unstable compounds are the intense coloration produced when the two constituents are mixed—a coloration which reaches its maximum when the proportions are 1 mol. : 1 mol., and analogy with the polynitro-derivatives, for Kremann has shown that both di- and trinitro compounds form compounds with amines, those of the trinitro-derivatives being the more stable.

**Halogen Derivatives of Oxides of Cresyl.**—A. Mailhe and M. Murat.—The mono- and di-halogen derivatives of the three cresyl oxides can readily be obtained by the action of chlorine or bromine on these ethers. The chlorine derivatives and the mono-brom derivatives are relatively stable, and can be distilled at the ordinary pressure without undergoing appreciable decomposition. The dibrom derivatives, however, which have been previously prepared by Cook are fairly easily decomposed.

**Formation of Sparteilene.**—Charles Moureu and Armand Valeur.—Methylhemisparteilene gives with methyl iodide a mixture of two isomeric iodomethylates. This mixture is transformed into the quaternary ammonium hydrate by the action of silver oxide, and this can then be decomposed by keeping it *in vacuo* at  $70^\circ$ , the product being dimethylhemisparteilene. Again, an iodomethylate is obtained by the action of methyl iodide, and the corresponding quaternary ammonium hydrate is decomposed *in vacuo* at  $75^\circ$ , giving sparteilene,  $\text{C}_{15}\text{H}_{20}$ . It is a colourless liquid boiling at  $157$ – $159^\circ$  under 18 mm. It has no rotatory power, and its molecular refraction agrees with the calculated molecular refraction for the hydrocarbon,  $\text{C}_{15}\text{H}_{20}$ , possessing six double bonds. Sparteilene is derived from spartein by the removal of two molecules of ammonia.

**Saccharification of Starch by Dilute Acids.**—A. Fernbach and M. Schoen.—The authors have studied the

action of dilute acids on starch, and have found that maltose is the first sugar formed; they have detected the maltose by obtaining its characteristic osazone, and determining its melting-point.

## MISCELLANEOUS.

**International Institute of Agriculture.**—The May number of the *Bulletin of Agricultural Statistics* has just been issued by the International Institute of Agriculture in Rome. The figures published in April with regard to the areas sown to winter cereals in the Northern Hemisphere are confirmed in the May number, additions having been made in the form of the areas sown in Italy (wheat, 4,750,000 hectares; rye, 122,000 hectares; barley, 245,000 hectares; oats, 500,000 hectares), and the area of wheat abandoned in the United States and Canada (United States, 20 per cent; Canada, 31 per cent). The weather during April has had a somewhat unfavourable effect upon vegetation, with the result that development is in general rather backward. The condition of the crops, however, on May 1st was, for the greater part good, except in the United States, where the condition figure was below that of the corresponding period in 1911. (Winter wheat 93 on May 1st, 1912, as against 100 on May 1st, 1911; winter rye 98 as against 100). The germination of spring wheat, rye, barley, and oats has been, on the whole, uniform except in Austria. In the May *Bulletin*, flax has been included for the first time in the list of products considered, information having been received this month from Belgium, Bulgaria, Ireland, Hungary, Italy, Roumania, Japan, and India. The general condition of the flax crop is good, the areas sown being as follows:—Belgium, 13,300 hectares; Italy, 8000 hectares; India, 1,402,135 hectares as against 1,255,115 hectares sown last year. Another culture considered for the first time in this number is silkworm rearing, information also being given as to the condition of the mulberry trees, which was satisfactory in Austria, Croatia and Slavonia, and Japan, and bad in Italy. The quantity of silk-worm eggs placed for incubation was in Austria 29,414 ounces of 30 to 36 grms.; in Bulgaria 14,336 hectogrms. or 96 per cent of last year's figure; and Japan, 521,000 hectogrms., the latter being 102 per cent of the amount placed for incubation last year. Information is also given in regard to vineyards, the vines having suffered in Austria, France, Hungary, and Italy through damage caused by the late hoar frosts. The *Bulletin* closes with the publication of the results of the live stock censuses in Argentine, Cuba, United States, and Egypt.

## MEETINGS FOR THE WEEK.

THURSDAY, 13th.—Royal Society. "Chemically Active Modification of Nitrogen produced by the Electric Discharge," by Hon. R. J. Strutt. "Series Lines in the Arc Spectrum of Mercury" and "Constitution of the Mercury Green Line  $\lambda = 5461 \text{ \AA}$ ," and on the Magnetic Resolution of its Satellites by an Echelon Grating," by J. C. McLennan. "Convergence of certain Series involving the Fourier Constants of a Function" and "Classes of Summable Functions and their Fourier Series," by W. H. Young. "Number of  $\beta$ -Particles emitted in the Transformation of Radium," by H. G. Y. Moseley. "Portland Experiments on the Flow of Oil," by S. D. Caruthers. "A Form of the Solution of Laplace's Equation suitable for Problems relating to two Spheres," by G. B. Jeffery. "Emission Velocities of Photo-electrons," by A. L. Hughes.

FRIDAY, 14th.—Royal Institution, 4. "Unknown Parts of South America," by A. Henry Savage Landor. Physical, 8. "Method of Determining very Small Differences of Density," by T. H. Blakesley. "The Maximum Sensibility of a Duddell Vibration Galvanometer," by H. F. Haworth. "Accurate Examination of the Steinmetz Index for Transformer Iron, Stalloy, and Cast-iron," by F. Stroude.



# THE CHEMICAL NEWS.

VOL. CV., No. 2742.

## SPITZBERGEN COAL.

By W. HAMILTON PATTERSON, M.Sc.

It is now generally known that coal, in apparently extensive deposits, occurs both in Arctic and Antarctic regions.

Attention having been called to the good properties for steam-raising purposes of Spitzbergen coal in particular, it was considered to be of interest to subject it to a thorough chemical examination. The result is interesting. The finely powdered coal showed, by reflected light, very distinct brown colour similar to German brown coals, but it was found to differ from them on further examination, in that it contained relatively little moisture and possessed a high calorific value. The latter is mainly due to its high hydrogen content; corresponding to the hydrogen it contains a large percentage of volatile matter.

The coal was found to be hard, and showed a very marked crystalline fracture when broken. A minute brown deposit was visible on the edges at a few places, but no sign of pyrites or calcium carbonate was to be seen.

The following gives the results of elementary analysis:—

|                          | Per cent. |
|--------------------------|-----------|
| Moisture (total) .. .. . | 1.99      |
| Ash .. .. .              | 2.52      |
| Carbon .. .. .           | 79.79     |
| Hydrogen .. .. .         | 5.45      |
| Sulphur .. .. .          | 0.76      |
| Nitrogen .. .. .         | 1.08      |
| Oxygen .. .. .           | 8.41      |
|                          | 100.00    |

On making a coking experiment the coal gave 65.20 per cent of coke; this was firm and blown out, and the gas evolved burnt with a large but not very smoky flame.

|                           | Per cent. |
|---------------------------|-----------|
| The volatile matter was.. | 32.81     |
| The fixed carbon .. ..    | 62.68     |

and from the analysis above the combustible matter was 95.49 per cent. From the above analysis the calorific value, calculated by the formula (which is that adopted in Germany)—

$$H = 81C + 290 \left( H - \frac{O + N}{8} \right) + 25S - 6W,$$

gives 7705 calories, or heat units (equivalent to 13,869 British thermal units), which is the heat evolved when the coal burns to carbon dioxide and steam.

The experimental calorific value determined by burning a sample of the coal in the bomb calorimeter under a large pressure of oxygen gave the gross calorific value 8034 calories, or heat units, which is the heat evolved when the coal burns to carbon dioxide and to liquid water at ordinary temperature.

|                                                                                                                   | Cals. |
|-------------------------------------------------------------------------------------------------------------------|-------|
| Correction for water condensed from oxidation of hydrogen and from moisture contained (hydroscopic water) .. .. . | 306   |
| Correction for formation of sulphuric acid .. ..                                                                  | 17    |
| Correction for formation of nitric acid .. ..                                                                     | 8     |
| Total correction .. .. .                                                                                          | 331   |

which gives 7703 calories (heat units) (or 13,865 British thermal units), the net value, corresponding to the value obtained by calculation above.

The coal therefore gives actual and calculated calorific values which are practically identical. With an ordinary brown coal one would expect a divergence between the true calorific value actually determined by the bomb calorimeter and that calculated from the above formula of more than 1 per cent, and probably up to 3 per cent.

A calculation of the amount of hydrogen from the volatile matter found, using the formula of Seyler, i.e.,  $H = 1.72 + 2.43 \log V$ , where H is the percentage of hydrogen and V the volatile matter in the dry and ash-free coal, or combustible portion, gives the hydrogen percentage as 5.45 per cent, or a value identical to that actually obtained by combustion.

These results would lead one to describe the Spitzbergen coal as being a very pure coal, if such a term may be applied to such a heterogeneous substance as coal is known to be.

The Monksferry Chemical and Fuel Laboratory,  
Birkenhead.

## THE PREPARATION AND PROPERTIES OF METALLIC CERIUM.\*

By ALCAN HIRSCH.

(Continued from p. 268).

### Preparation of Anhydrous Chlorides (continued).

IN view of the fact that the non-aqueous methods were not suitable for the problem at hand, resort was again made to dehydration methods. It was found that by treating the mixed oxides with concentrated HCl, evaporating to dryness, adding more HCl, and repeating the process a number of times, a product was obtained corresponding to one of the lower hydrates of the chlorides. This white solid was very hygroscopic, and dissolved in water with avidity and evolution of considerable heat; when broken into lumps and calcined at a low temperature (not exceeding 125°) on an asbestos-covered hot plate, further dehydration occurs without decomposition. The heating should be continued for a long time (about twelve hours), and the temperature must be kept low. If these directions are followed, a product corresponding approximately to the monohydrate is obtained. The great difficulty is to get rid of the last molecule of water, which is the most tightly bound of all, without decomposing the chlorides.

Matignon (*Ann. Chem. Pharm.*, 1906, [8], viii., 364; *Comptes Rendus*, 1902, cxxxiv., 1308) and Bourion (*Ann. Chem. Pharm.*, 1910, [8], xxi., 49; Matignon and Bourion, *Comptes Rendus*, 1904, cxxxviii., 631) have done a great deal of work on the preparation of anhydrous chlorides. They have found that certain chlorides of the metalloids, especially those of phosphorus and sulphur, act as catalysts in the dehydration of hydrated chlorides, and that in the presence of dry HCl gas, chlorine and sulphur monochlorides (S<sub>2</sub>Cl<sub>2</sub>), the chlorides of silicon, aluminium, thorium, neodymium, praseodymium, samarium, and vanadium can be prepared in the anhydrous condition.

For the problem at hand this method had apparently many advantages and few disadvantages, chief of which was the very disagreeable nature of sulphur monochloride. It was resolved therefore to try out this method on the preparation of the anhydrous mixed chlorides. About 400 grms. of the hydrated chlorides were placed in a porcelain tube furnace through which was passed a mixture of chlorine, S<sub>2</sub>Cl<sub>2</sub>, and HCl gases. The maximum temperature was about 300°, and the heating was continued for two and one half hours. The product in the centre of the tube was fritted together, and a sample for analysis was

\* A Paper presented at the Twentieth General Meeting of the American Electrochemical Society, Toronto, Canada, September, 1911. From the *Journal of Industrial and Engineering Chemistry*, iii., No. 12.

taken from this portion; 1.4 per cent was insoluble, and the chlorine content of the soluble part was 42.4 per cent—the per cent of chlorine in  $\text{CeCl}_3$  is 43.2 per cent. The product melted satisfactorily, and the method seemed suitable, so that a plan was devised for its application on a larger scale.

A terra-cotta drain-pipe 4 inches (10 cm.) in diameter and 4 feet (1.2 m.) in length, was fitted at both ends with graphite caps, through which passed short pieces of glass tubing, two at one end and one at the other. The furnace was a circular-flame tube furnace in which the pipe could be heated gradually and uniformly, and the temperature was under positive control. The monohydrated chlorides, prepared by the method previously described, were dehydrated, about a kilogram. at a time. The salt was spread evenly in the pipe, in a layer about  $\frac{3}{8}$  inch (2 cm.) thick. The caps were then inserted, and the ends heavily luted with a mixture of magnesia, asbestos fibre, cement, fire-clay, and water, and allowed to dry, when a joint practically gas-tight was obtained. Dry  $\text{HCl}$  gas was passed over the chlorides, and as soon as the air was displaced the heating was commenced with a small smoky flame. After the tube was warm, chlorine and  $\text{S}_2\text{Cl}_2$  vapours, as well as dry  $\text{HCl}$ , were passed through the tube, and the temperature was gradually raised to just below  $400^\circ$ . The dehydration is completed in about three hours if the temperature is correctly adjusted, but may take longer. The anhydrous chlorides are placed, while still warm, in dry bottles, and the corks paraffined in. Care must be taken to prevent the sewer-pipe from cracking when being heated, and this tendency forms one of the principal weaknesses of the process. A metallic container cannot be used in the dehydration on account of the highly corrosive action of the vapours.

The sulphur monochloride seems to catalyse the dehydration process, and has the further function, together with the chlorine gas, of re-converting to chloride any oxide or oxychloride which may form. If the temperature is too high, oxide or oxychloride may form even in the presence of chlorine and sulphur monochloride. The dehydration may be carried out by  $\text{HCl}$  gas alone, and a scheme was devised for preparing pure anhydrous cerium chloride using this method. Since the process was the outcome of much work and of experience in the handling of the chlorides, it is described here in some detail.

The double cerium ammonium nitrate from the fractionating vats, where it has been purified and separated from the other rare earths by fractional crystallisation, was used. The absorption spectrum of a concentrated solution of the nitrates showed only the faintest traces of the neodymium and praseodymium bands. The contents of a large bottle containing 5 kilograms. of the double nitrates was divided into four portions and placed in 14 inch (35 cm.) porcelain evaporating dishes. The dishes were filled with concentrated  $\text{HCl}$ , and placed on steam-heated sand-baths. Each dish was suitably protected from drippings from the hood by wooden covers raised a few inches above the tops of the dishes and supported on silica bricks. Fresh acid was added daily as required, and the evaporation continued for about three weeks, at the end of which time the nitrates had been completely converted to chlorides and all the ammonium salts had been expelled. The white solid was broken into lumps, and heated on an asbestos covered hot plate to convert it to the monohydrated chloride. The final dehydration was carried out as follows (see Fig. 1):—About 400 to 500 grms. were placed in a 10 inch porcelain evaporating dish. A short stem funnel about 9 inches in diameter was inverted and placed over the salt. A layer of asbestos fibre was packed tightly around the outside edge of the funnel, and plaster of paris set over this. A glass tube passing through the stem of the funnel and reaching to just above the layer of chloride conducted in the dry  $\text{HCl}$  gas, which was passed at a rapid rate over the heated chloride. The salt was stirred around from time to time by means of a long thick glass rod. The heating was done gradually, and the pro-

gress of the dehydration could be watched, through the glass funnel, and its completion checked nicely. The anhydrous chloride was placed, while still warm, in dry glass vessels, and the corks paraffined in to exclude moisture from the extremely hygroscopic product.

The chloride prepared by this method melts to a clear limpid liquid, and is suitable for electrolysis. The process meets practically all the requirements—it gives a suitable product, it is rapid, inexpensive, and simple, the progress and completion of the dehydration can be watched, overheating may be avoided, and large amounts of chloride prepared in the minimum amount of time. Chlorine and sulphur monochloride may be used in addition to the dry  $\text{HCl}$  gas, but this was not found necessary, as the water was driven off rapidly and completely without their presence.

It was observed that the anhydrous rare earth chlorides may be partially converted into oxides or oxychlorides if they were carelessly heated in the presence of air. For this reason experiments were conducted on melting the chlorides in a non-oxidising atmosphere in a Rose crucible. In the presence of carbon dioxide some oxychloride was formed, and in an atmosphere of carbon monoxide a crust of brownish oxide appeared.

The best method of melting the anhydrous chlorides without decomposition was found to be by heating a small portion in a covered crucible until a clear melt was obtained,

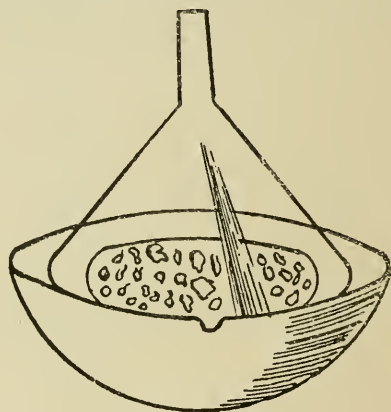


Fig. 1.

and then introducing successive small portions of the chlorides to the melted portion. In this manner circulation of air is avoided, as the crucible is kept covered. A good way is to first melt sodium or potassium chlorides, or a mixture of these, and then to add small amounts of the rare earth chlorides, keeping the crucible covered as much as possible. A small amount of oxide or oxychloride will "gum up" the entire melt, and for electrolysis this condition must be carefully guarded against.

#### Preparation of Anhydrous Fluorides.

Another salt required in large amounts was the anhydrous mixed fluorides,  $\text{RF}_3$ . This preparation involves some of the difficulties encountered in the preparation of the anhydrous chlorides. The fluorides are more stable and less hygroscopic than the chlorides, but they are more corrosive in their action on apparatus. Porcelain vessels cannot be used, and one is almost entirely limited to lead vessels in the preparation of these fluorides. However, lead linings are easily placed in evaporating dishes, especially in the large enamelled iron ones, and five gallon jars made of lead containing 10 per cent antimony were found very convenient in this work.

A few methods are found in the literature for the preparation of anhydrous cerium fluoride,  $\text{CeF}_3$ , but not many. The fluorides of cerium, especially the hydrated



ones, are insoluble in water, and are gelatinous precipitates usually obtained by double decomposition.

The tetrafluoride,  $\text{CeF}_4 \cdot \text{H}_2\text{O}$ , is found in nature as fluoroceric, and when this mineral is heated it decomposes, forming the impure anhydrous fluoride,  $\text{CeF}_3$  (Brauner, *Monatsh. Chem.*, 1882, iii., 1). By precipitating cerous nitrate with hydrofluoric acid Jolin (*Bull. Soc. Chim.*, 1874, [2], xxi., 533) obtained a gelatinous precipitate, which after drying over sulphuric acid corresponded to the formula  $2\text{CeF}_3 \cdot \text{H}_2\text{O}$ . When this substance was heated it decomposed, leaving a residue of oxide.

In the preparation of the anhydrous rare earth fluorides both dry and wet methods were tried. Hydrofluoric acid gas was passed over a small amount of the pulverised carbides placed in an iron tube, and heated to a temperature of about  $200^\circ$ . The hydrofluoric acid gas was prepared by heating  $\text{CaF}_2$  with concentrated  $\text{H}_2\text{SO}_4$  in a copper retort. Some fluoride was formed, but was contaminated with carbon and undecomposed carbide, and the method was regarded as unsuccessful.

The action of concentrated HF on the oxides was tried. A small amount of the mixed oxides was heated in a platinum dish with successive portions of concentrated HF. The action was vigorous at first, but soon stopped, and the residue was a mixture of oxide and fluoride.

As the anhydrous fluorides were required, a process in which no water was used obviated the subsequent removal of that water, and seemed to be at least worthy of trial. The chlorides were boiled with absolute alcohol until a concentration solution was obtained, which was transferred to a lead tub placed in hot brine, so that the precipitation might be done from a hot solution, and HF gas passed into the hot chlorides. The objections to this method are that the fluorides so prepared are contaminated with some chloride. Furthermore, the saturation of the hot alcohol with HF gas is a very slow process, and the fluorides are extremely difficult to filter on account of their gelatinous nature. If the precipitation is done in the cold, the fluorides come down in a slimy condition almost impossible to handle, hence the reason for precipitating from hot solution. While the precipitation may be done by the action of a concentrated solution of hydrofluoric acid on the aqueous solution of the chlorides, the fluorides settle far less readily in water than in alcohol. Consequently, on account of the above reasons, the next modification in the process was to dissolve the mixed oxides in concentrated HCl, concentrate the solution, and add the requisite amount of concentrated HF to the hot solution. After allowing the precipitate to settle, the supernatant liquid was syphoned off, alcohol added, the whole stirred thoroughly, the precipitate allowed to settle, the liquid syphoned off, and the treatment with successive portions of alcohol repeated several times. The fluorides were dried at a low temperature and were pink in colour. They melted at a fairly high temperature (about  $900-1000^\circ$ ) to a clear liquid, and the process was satisfactory except for the time required for the precipitates to settle.

In order to flocculate the fluorides so that they could be more easily filtered, the precipitate of the fluorides was placed in a round-bottom Jena flask about half full of absolute alcohol, and heated in an autoclave at a temperature of  $130^\circ$  and a pressure of 90 pounds per square inch. The product so treated seemed to settle somewhat more rapidly, but filtered very slowly indeed.

After many trials, the most satisfactory preparation of the anhydrous fluorides was found to be best effected by the following method:—About a kilogram. of the mixed oxides was placed in large porcelain evaporating dish, and digested in a steam closet with concentrated HCl until a clear concentrated solution of the chlorides was obtained. The hot solution, containing only a slight excess of hydrochloric acid, was transferred to a five-gallon lead jar, and concentrated HF added to complete precipitation. The fluorides were allowed to settle somewhat, as much of liquid syphoned off as was possible, and washed twice with hot water and several times with 95 per cent alcohol.

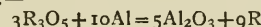
Only a few minutes' time was allowed after each washing for the precipitate to settle. The fluorides were then placed in a lead-lined cage centrifuge, and most of the remaining alcohol removed in this manner. Absolute alcohol was added, and the solution evaporated to dryness without decanting. The absolute alcohol dehydrates the centrifuged fluorides very well. They were then dried at  $100^\circ$ , and the temperature raised to  $200^\circ$  at the end. About 6 kilograms. of the fluorides were prepared in this manner. The process is a fairly satisfactory one, and as no filtering is done, the method is fairly rapid.

### Preparation of Metallic Cerium and Mischmetall.

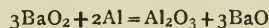
#### Thermal Reductions.

Thermal reductions were tried in the hope of producing rare earth metals by this simple means. Previous work of this nature has already been referred to (Marignac, *Ann. Chem. Pharm.*, 1849, [3], xxvii., 209; Wöhler, *Liebig's Ann.*, 1867, cxliv., 251; Winckler, *Ber.*, 1891, xxiv., 873; Matignon, *Comptes Rendus*, cxxxi., 837; Schiffer, "Versuche zur Reduktion d. Cerit-oxygen mit Al," Dissertation Tech. Hochschule, München). Magnesium and calcium shavings and aluminium powder were used as reducing agents on the mixed oxides. These experiments were conducted in electrically-baked magnesia linings placed in graphite containers. Carbon and silicon were also used to reduce the oxides, but external heat was applied to give the high temperature required. No metal was formed in these last instances, but the carbides and silicides respectively. The carbide,  $\text{RC}_2$ , is pyrophoric, but the silicide,  $\text{RSi}_2$ , is not. Reductions using magnesium and calcium in excess gave alloys, many of which were pyrophoric.

Several trials to reduce the oxides with aluminium are here recorded:—



150 grms. mixed oxides require 27 grms. aluminium.



507 grms. barium peroxide require 54 grms. aluminium.

The following charge was weighed out, intimately mixed, and fired by means of magnesium wire and thermit igniter:—

|                          | Grms. |
|--------------------------|-------|
| Mixed oxides .. .. .     | 150   |
| Aluminium powder .. .. . | 40    |
| Barium peroxide .. .. .  | 120   |

The reaction was vigorous, but not violent. A 5 gm. lump of metal and many small globules were obtained. The specific gravity of the metal was greater than that of aluminium.

In another experiment the following charge was used:—

|                               | Grms. |
|-------------------------------|-------|
| Mixed oxides .. .. .          | 200   |
| Aluminium powder .. .. .      | 61    |
| Barium peroxide .. .. .       | 200   |
| Black thermit mixture .. .. . | 50    |

The black thermit was used to produce a higher temperature, and also for the reason that the affinity of cerium for iron was thought to be greater than that of cerium for aluminium; 35 grms. of hard brittle alloy were obtained, but the content of rare earth metals was low.

In the case of these thermal reductions, either an alloy, a compound, or a lower oxide of the rare earths was obtained. Owing to the high heat of formation of these oxides, the failure of aluminothermics in the production of metal was only to be expected. The writer believes that a study of the equilibrium conditions of these reactions would form an interesting and valuable research, and might result in the discovery of lower rare earth oxides.

*Earlier Work on the Electrolysis of the Anhydrous Chlorides.*

The previous work on the electrolytic preparation of cerium has already been referred to. The method of Bunsen, which the earlier investigators used, is described as follows (Moissan, "Chimie Minérale," vol. iii., 823:—"In a porcelain crucible, in which the mixed chlorides of sodium and potassium has been melted, small amounts of anhydrous cerium chloride were introduced by means of a small porcelain spatula. An annular piece of iron was used as anode, and the cathode consisted of a platinum wire, protected by a short piece of clay-pipe stem. The temperature of the fused bath was lowered until a thin crust formed on the surface of the bath, when the electrolysis was commenced. Globules of cerium rose to the surface and burned with explosive force. Hillebrand and Norton thus obtained metallic globules to the amount of 6 grms."

At one time the writer tried to duplicate the above experiment, but was unable to collect any metal. The platinum cathode was badly attacked; in fact, part of it melted off, due to formation of an alloy with cerium.

For a survey of Muthmann's work on the rare earth metals the reader is referred to the original reference (Muthmann, Hofer, and Weiss, *Liebig's Ann.*, 1902, cccxx., 231; Muthmann and Weiss, *Ibid.*, 1904, cccxxxi., 1; Muthmann and Beck, *Ibid.*, 1904, cccxxxi., 46; Muthmann, Weiss, and Scheidmandel, *Ibid.*, 1907, ccclv., 116). The type of vessel used in the electrolysis of the chloride is shown in Fig. 2, and is now generally known as the Muthmann cell. It is a semi-water jacketed vessel, constructed of copper, and may be used with or without the heating circuit. The principal objection which the writer has to the cell is its complicated nature. The cathode should be insulated carefully, and this is difficult, as the asbestos packing is attacked by cerium metal, and during the course of the electrolysis the insulation is apt to be destroyed, and the walls of the vessel may act as cathode, with the subsequent contamination of cerium with copper. This is especially liable to occur if the temperature of the bath is too high. The heating circuit must also be insulated from the walls, and the carbon heating rods are liable to crack and break. Unless the contents of the cell are poured or tapped at the completion of the electrolysis, the entire cell has to be dismantled after each run. When worked on a small scale, the manipulation of this electrolytic cell is a troublesome and difficult operation.

In the present research, numerous runs were made before more than traces of metal were obtained. It is believed by the writer that an account of failures is often fully as important as that of successes, as it is only by correction of faults that successful results are obtained. Therefore a brief account of the earlier unsuccessful attempts to produce rare earth metal are here given. It was only by a complete understanding of the reasons for failure that a successful solution of the problem was accomplished.

The different types of cells used where anhydrous mixed chlorides were employed as the electrolyte are shown in Figs. 3 to 5. (The crucible shown in Fig. 4 was split longitudinally into two sections, which were cemented together by graphite molasses paste and clamped firmly together. This makes a very convenient form of electrolytic cell, as it can be easily dismantled and also very quickly re-assembled). They were all constructed of the same material, graphite. The anodes were of graphite, but in the case of the insulated cathodes these were sometimes of graphite and sometimes of iron. In many cases where a graphite crucible was used as both containing vessel and cathode, the melting was done in a resistor furnace, and then the electrolysis was begun. In some instances the heating was done by alternating current, and could be maintained and regulated during the course of the electrolysis. The melting of the electrolyte was sometimes done by a small thin carbon heating rod placed between electrodes, as shown in Fig. 2. An arc could not

be used to melt the chlorides, as they are decomposed at that temperature.

The principal difficulties encountered in these experiments were the following:—

1. The salt would not melt to a clear liquid.
2. The electrolyte would remain liquid for a time, but would eventually solidify.
3. The IR drop across the cell, and the ampèreage would vary.
4. The anode would not functionate properly.

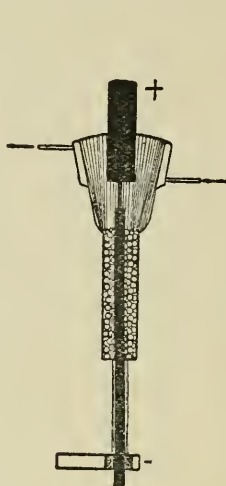


Fig 2

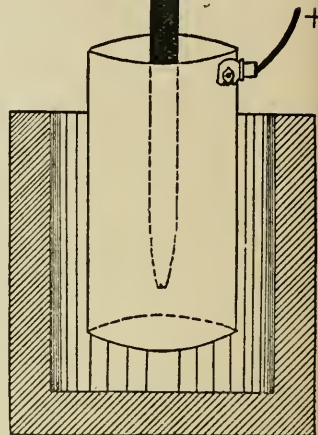


Fig 3

5. On completion of the electrolysis, no regulus of metal was obtained.

6. Minor difficulties, such as short-circuiting of insulated cathodes, leakages, fracture of electrodes, &c., liable to happen in any fused electrolysis, were encountered.

The reasons for the above difficulties were found by experience to be explained as follows:—

1. If the chlorides did not melt to a clear liquid, then either the chlorides were not anhydrous or they were

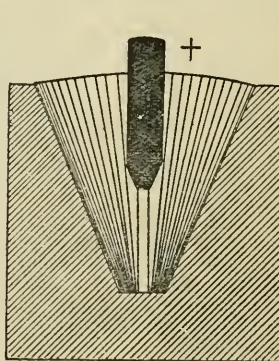


Fig 4

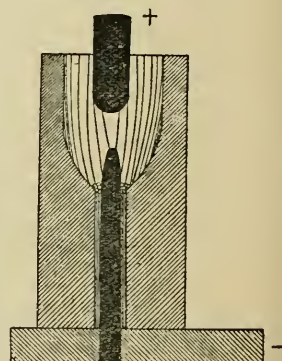


Fig 5

decomposed in the process of fusion. The proper manner of melting the chlorides has already been discussed in sufficient detail.

2. The "gumming-up" was caused either by the formation of a higher melting salt, as the oxide or carbide, or the temperature of the bath was too low (see 4, below).

3. As the generator voltage and the external resistance were constant, changes in the voltage across the cell and the ampèreage were caused by a variation of the internal



resistance of the cell. This variation was caused by the following factors:—Change in temperature of the bath; depletion in the electrolyte, or segregation, such as double layers, &c.; formation of intermediate products of varying resistance, such as sub-chlorides; differences in thermal conductivity of the electrolyte at different stages of the electrolysis, &c. It was found that the potential difference and the ampère of any one cell can vary only between certain limits for successful electrolysis. The heating value of the current ( $C_2R$ ) in cases where no external heat is applied must be such as to keep the temperature of the bath at a certain value. If the temperature of the electrolyte is too high, it is impossible to successfully electrolyse in the case of cerium chloride.

4. The function of the anode was (1) to cause the separation of chlorine, and (2) to supply most of the heat necessary to keep the bath fused.

(1) In all these experiments the ampère was such that, if the cell was working properly, there was a copious evolution of chlorine gas. In many cases the voltage across the bath and the ampère would be approximately the proper values, and yet very little chlorine would be evolved. This may occur under several very different conditions. If the temperature of the bath is low, the semi-fused chloride is a very good conductor, and the entire bath may behave as a conductor of the first-class. In this case practically no chlorine will be evolved. Again, if the temperature of the bath is too high, little chlorine is given off. This is due to the fact that at the cathode the chloride is partially reduced to sub-chloride, which diffuses to the anode, and is there oxidised by the chlorine to chloride. There is a narrow limit of temperature where true electrolysis occurs; that is, where anhydrous  $CeCl_3$  is decomposed by the current to metal and chlorine.

(2) In cases where the containing vessel acted as the cathode, anodic current density was much greater than the cathodic, consequently most of the heat was supplied to the cell by the anode. In the preliminary experiments the anodes were of graphite, but with the same diameter anode and the same current the heating is greater with a carbon than with a graphite anode. In some of the later runs carbon was used as the anode material for the reasons mentioned above. If the diameter of the anode is too great, a large current is required to keep the bath molten. Besides, the anode is brought nearer the walls, and most of the current may pass through the upper part of the cell. This should be avoided, as the path of least resistance for the current should be from the anode to the bottom of the cell, as this ensures good circulation of the electrolyte and the deposition of the metal in a united form. If metal is deposited on the upper walls, some is apt to become oxidised by contact with the air, and this may result in the bath becoming viscous.

5. Many of the reasons for failure to obtain a regulus of metal have been given above. The metal may be deposited in a finely-divided unfused condition, and may be disseminated throughout the body of the electrolyte. It may be totally or partially soluble in the electrolyte (for instance, Li in  $LiCl$ ), or the metal may react with the products at the anode (as chlorine), or the material of the cell (with copper forming an alloy, or with graphite forming a carbide).

(To be continued)

**A Laboratory Adhesive Medium.**—This may be made by charging unskimmed condensed milk with sufficient dextrine to form a homogeneous liquid medium. It forms a perfectly safe adhesive medium for paper, and it will keep.—J. C. THOMLINSON, B.Sc.

**Royal Institution.**—A General Monthly Meeting of the Members of the Royal Institution was held on the 3rd inst.; the Duke of Northumberland, K.G., President, in the Chair. Miss M. W. Hughes, Mr. Charles H. Merz, Mr. Oscar Schwartz, and Mr. J. D. Walker, K.C., were elected Members.

## A PASTE FOR THE NOTE BOOK.

By JOHN H. EGGERS.

THE very interesting discussion started by R. Stuart Browne on the subject of filing notes recalls to me some of my experiences in the matter of finding a suitable paste for pasting clippings in a scrap-book—a system of keeping notes which I at one time employed, but which I was compelled to discard for about the same reasons advanced by Mr. Browne.

The pages of the scrap-book in which I kept my clippings were of heavy manila paper, but notwithstanding this, I noticed that they frequently had a tendency to wrinkle after the paste had been applied. This not only had the effect of increasing the thickness of the book, but it detracted very much from its appearance. It occurred to me that the wrinkling was largely due to the character of the paste used, and inasmuch as I had used at various times different kinds—from the home-made variety, consisting of flour and water, to the finest grade of library and photo-mounting paste, each of which seemed to affect to a different degree the amount of wrinkling—I thought it might be interesting to make a number of experiments with different kinds of paste and to study their effect.

It was just as I surmised. The ordinary flour pastes produced the maximum amount of wrinkling, while the expensive library pastes, when a little care was paid to the amount of water used for softening, left a neat smooth page. It must not be thought, however, that it was impossible to obtain good results with flour paste. For some reason, which I could never fathom the cause of, some of the batches of paste which I made and experimented with gave just as good results as the best library paste, while the library pastes, if thinned with too much water, were just as bad as the poor flour pastes.

My next step was to learn how to make the so-called library paste, but here I encountered an obstacle. These pastes, of which there are only a few kinds on the market, are all supposed to be made by secret processes, and although their general composition is well known, the details of the process of manufacture are more or less of a mystery. In the various books on chemical technology which I consulted, I found a great many ideas advanced about them, and the only definite information which I could glean from them was that they consisted of dextrine and a preservative. Inasmuch as dextrine is a very peculiar substance, possessing various properties according to the temperature at which it is handled, I soon learned that solving of the secret of making a library paste was a problem of no mean proportion. Finally, when I had about given up all hopes of stumbling on the process, I came across the clue in a popular magazine, and my experiments soon demonstrated that I had the secret. I have been making and using this paste now for some time, and I can vouch for the excellent results to be obtained with it, and I have no doubt whatever but that it is the identical paste which is prepared and sold under the trade names of library and photo-mounting paste. When properly thinned with water, it may be used for scrap-book work or pasting clippings on loose leaves, as described by Mr. Browne, and it will leave a perfectly smooth page on drying. The following is the formula for making this paste:—White dextrine,  $2\frac{3}{4}$  lbs.; water at  $160^\circ F.$ , 2 qts.; oil of wintergreen, 0.8 cc.; oil of clove, 0.8 cc.

Bring the water to  $160^\circ F.$  and stir the dextrine in slowly, taking care not to allow the temperature to vary more than  $1^\circ$  either way until the dextrine has dissolved to a perfectly clear solution. As soon as the dextrine has passed into solution, add the essential oils slowly, stirring all the time. After this has been done, allow the solution to cool, and then pour it into bottles and cork. These bottles must then be set aside for a week or two, to permit the paste to congeal. As soon as the paste "sets," it will have a perfectly white colour, and will possess the firm consistency which is characteristic of library paste. In

order to use it, it is necessary to add a little water, and work it around with a brush.

In preparing this paste care should be taken to use the best grade of white dextrine. The whole secret of the process of manufacturing is in maintaining the temperature at 160° F. At this temperature the dextrine undergoes certain peculiar molecular changes, and any serious variation from it results in a very inferior product.—*Transactions of the American Metallurgical Society.*

### "RED RAIN" DUST.\*

By THOS. STEELE, F.L.S., Sydney.

In 1898 I communicated to this Association an account of an examination of a sample of dust which fell in Victoria in December 1896 (*Australasian Assoc. Adv. Science*, 1898, vii., 334). On the morning of October 11th, 1909, a similar dust-shower occurred over Sydney and surrounding districts, the fall being subsequent to a period of strong westerly winds. Although a fair amount of rain fell just before that carrying the dust, the latter was brought down by a moderate shower, immediately after which the weather became fine, so that much of the dust remained, adhering to railings, roofs, leaves of plants, footpaths, &c., where it quickly dried. On the morning of the fall I was able to gather a fair quantity of the dust from flat skylight windows and from gutters on the roofs of buildings at Pyrmont, a suburb of Sydney. The dust which was deposited on the flat skylight windows had to a large extent accumulated in a line along the lower edge of the glass, and by scraping this off into a sheet of paper a very clean sample, quite free from soot and other contamination, was obtained for analysis. The dust was examined by boiling with hydrochloric acid, the solution being treated in the manner usual in such analyses. The results obtained were:—

Sample dried at 110° C.—

|                                 |        |
|---------------------------------|--------|
| Organic matter, &c. (a) .. ..   | 8.37   |
| Sand and insoluble .. ..        | 69.11  |
| Soluble silica .. ..            | 0.10   |
| Ferric oxide .. ..              | 5.05   |
| Ferrous oxide .. ..             | 0.52   |
| Alumina .. ..                   | 14.76  |
| Lime .. ..                      | 0.56   |
| Magnesia .. ..                  | 0.95   |
| Sulphuric anhydride .. ..       | 0.14   |
| Phosphoric oxide .. ..          | 0.22   |
| Not determined .. ..            | 0.22   |
|                                 | 100.00 |
| (a) Containing nitrogen .. ..   | 0.17   |
| Moisture in air-dried sample .. | 5.87   |

In composition and appearance this dust closely resembles that which fell in Victoria in 1898, both being doubtless derived from the dry interior of the continent. Neither of these dusts contained any magnetic particles.

An analysis of the Sydney dust by Mr. L. Cohen, published in the *Sydney Daily Telegraph* newspaper, Nov. 1st, 1909, shows the very large proportion of 14.69 (when calculated to dryness) of ferric oxide, no ferrous oxide, and considerably less alumina than I find to be present in my sample. So great a proportion of iron oxide may perhaps be due to contamination with rust from the iron roof on which Mr. Cohen's sample was collected.

A rough idea of the amount of dust which fell may be gathered from the weight collected by me from one of the skylight windows. To all appearances the greater part of

the dust which fell on the window remained adhering to the edge of the glass, though probably some was washed away. The window in question had an area of about 68 square feet, and the weight of air-dried dust collected therefrom was about 6 grms. This is equivalent to about 8½ lbs. per acre, or nearly 2½ tons per square mile.

Leaves of trees and various plants were coated with the dust, which collected along the veins and edges in such situations as would retain adhering water. As the water evaporated, the dust remained and was in evidence for several days until washed off by subsequent rain. Although the dust is spoken of as red, it is really of a pale buff or clay colour, which becomes somewhat red on moistening.

Some time after the publication of my paper on the Victorian dust of 1896, Dr. T. L. Phipson, of London, published two papers detailing the results of his examination of a small sample from the same fall, given to him by Captain C. J. Gray, who personally collected it (*CHEMICAL NEWS*, 1901, lxxxiii., 159, 253). Dr. Phipson claims to have detected nickel in the dust, which he estimates at about 1 per cent, and in his first paper he concludes that "it is partly, if not wholly, of cosmic origin, and not merely desert sand uplifted by the wind, nor volcanic dust; it would appear to be the mineral dust left in the higher regions of the air by the explosion of meteors or shooting stars." In his second paper, however, after examining a further sample weighing about half a grm., given him by Captain Gray, Dr. Phipson altogether ignores his first conclusion, and says:—"I am decidedly of opinion, after due discussion of this subject, that this dust brought down in the rain is of volcanic origin."

Working on much larger quantities than Dr. Phipson had at his disposal I have been unable, by ordinary chemical tests, to confirm his detection of nickel, the presence of which, in any case, is by no means a reliable indication of cosmic origin. I see nothing in the character of the dust or in the circumstances attending its fall to lead to any other conclusion than that it consists of ordinary soil, raised and carried by wind from the interior of Australia.

Prof. Liversidge, in 1902, published a most comprehensive and valuable paper on "Meteoric Dusts" (*Proc. Roy. Soc., N.S.W.*, 1902, xxxvi., 241; and *CHEMICAL NEWS*, 1903, lxxxviii., 16), on p. 283 of which he shows that the presence of nickel and cobalt in such dusts has no particular significance as an indication of cosmic origin.

A paper by T. L. Patterson, entitled "Recent Dust Showers" (*Illust. Sci. Monthly*, July, 1884) gives an interesting account of dusts collected by melting surface snow, and of certain curious fused spherules, some of which consist of silicates and others of magnetic oxide of iron, which occur in the smoke emitted by factory chimneys, and which were found by Mr. Patterson in the dust recovered from snow collected in the vicinity of a manufacturing town. Both kinds of spherules occur freely in the fine dust of factories burning coal, and when found in atmospheric dust those of magnetic iron oxide might, without this knowledge, be readily attributed to a cosmic source (see also *Brit. Assoc. Adv. Science Reports*, various volumes, 1881 to 1889, under "Meteoric Dust").

In 1901 Prof. Hartley and H. Ramage published an account of a careful spectroscopic examination of a large number of dusts from various sources (*CHEMICAL NEWS*, 1901, lxxxiii., 157), having special reference to the presence of small amounts of nickel and the rarer elements. One of the most striking features of this research was the demonstration of the constant presence of minute quantities of nickel and other rare metals in dusts from the most varied terrestrial sources. The composition of the sooty particles which form a conspicuous constituent of much of the atmospheric dust of our cities is fully dealt with by Prof. E. Knecht in a paper published in 1905 (*CHEMICAL NEWS*, 1905, xci., 259).

I exhibit samples of the Victorian and Sydney dusts and of leaves incrustated with the latter, also volcanic dusts from eruptions of Mounts Pelée and Vesuvius.

\* A Paper read before the Australasian Association for the Advancement of Science, Section B, April 3, 1912.



PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, May 23rd, 1912.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

*"Theory of a New Form of the Chamber Crank Chain."*  
By H. S. HELE-SHAW, F.R.S.

The paper commences by showing in what way the mechanism is derived from the ordinary type of crank mechanism, its various phases being indicated diagrammatically. One feature of the mechanism, which is of practical importance, is that the crank is fixed, and so a variable stroke can be obtained by very simple means. The new feature of the mechanism, which results in somewhat remarkable properties, is the employment of what is called "a floating guide ring." This device largely reduces the friction of the contrivance when working under high pressures. An analysis of this mechanism is given and the expression for the reduction of loss by this mechanism, both in ordinary friction and in churning by liquid friction losses. A particular example is given, and results are plotted graphically of a series of tests in which the data obtained from the use of a floating ring are compared with tests of a mechanism without such a device.

*"A New Treatment of Optical Aberration."* By Prof. R. A. SAMPSON, F.R.S.

*"On the Extinction of Light by an Illuminated Retina."*  
By Sir W. DE W. ABNEY, K.C.B., F.R.S.

In this communication the author describes an apparatus adapted for illuminating the retina with known amounts of light, coloured or white, and for extinguishing the sensation of the light in the different colours of the spectrum. Confining himself to the stimulation of the retina by white light only, he shows the movement in the spectrum of the rays requiring the maximum amount of diminution to extinguish their light according as the retina is more or less illuminated.

*"Optical Determinations at High Pressures."* By WALTER WAHL, Ph.D.

*Diagram of State of Carbon Tetrabromide.*—The melting-point of  $\text{CBr}_4$  is raised  $1^\circ$  by a pressure of 16 kg.  $\text{cm}^2$ . The transition-point from monoclinic to regular crystal form is raised  $1^\circ$  by 32 kg.  $\text{cm}^2$ . The melting-point curve and the transition-point curve do not, therefore, intersect at high pressures to form a "triple-point." In consequence the monoclinic form of carbon tetrabromide cannot be caused to melt at any temperature or pressure whatever.

*Diagram of State of  $\alpha$ -B-Dibrompropionic Acid.*—Two modifications of the acid are known, a stable one melting at  $64^\circ$  and an unstable melting at  $51^\circ$ . The unstable modification is not spontaneously transformed into the stable one so readily as in most other cases of "monotropy," and as only very small quantities are employed for these optical determinations, it has been possible to determine the melting-point curve of the unstable modification also. In consequence of the small velocity of crystallisation and of melting of both modifications, it has also been possible to determine the limits within which not only supercooling but also superheating can be effected. During isothermal melting of the unstable modification the pressure may be reduced as much as about 150 kg.  $\text{cm}^2$ , below the true melting-point pressure before melting takes place rapidly. This pressure difference corresponds to a superheating of  $2.5^\circ$ .

The melting-point of the stable modification is raised  $1^\circ$  by a pressure of 51.3 kg.  $\text{cm}^2$ . The melting-point curves thus run further apart as the pressure increases, and the modification unstable at ordinary pressures remains unstable at all pressures. If we continue the melting-point curves

towards negative pressure we find that they intersect at the absolute zero. The difference between the absolute melting-points of the two polymorphic modifications is therefore at any pressure similar to the difference between the absolute melting-points at ordinary pressure.

*"Changes in certain Absorption Spectra in Different Solvents."* By THOMAS RALPH MERTON, B.Sc. (Oxon).

1. The absorption spectra of uranous chloride in a number of organic solvents have been measured quantitatively, the results indicating that the differences cannot be considered as a shift of the bands, since the entire character and intensity of the absorption varies in different solvents.

2. The apparent gradual shifts observed when one acid radicle is replaced by another can be simply explained by the superposition of absorption curves, and evidence has been found in support of this explanation.

3. A marked change in the character of the absorption has been found in the presence of free acid, more especially in solvents containing a ketone group. The addition of another solvent to these solutions causes a slow disappearance of the lines without shift, in accordance with the results of Jones and Strong.

4. The influence of pressures up to 750 atmospheres on the absorption spectra of solutions has been investigated with negative results.

*"Changes in the Absorption Spectra of 'Didymium' Salts."* By WALTER C. BALL.

The absorption spectra given by aqueous solutions of "didymium" salts, such as the nitrate, chloride, &c., were observed to be considerably altered by sodium hyposulphite,  $\text{Na}_2\text{S}_2\text{O}_4$ , the lines and bands being altered in position, width, and intensity. These alterations were found to be independent of any reducing action of the very strongly reducing hyposulphite, but to be connected with changes in the ionisation of the didymium; for similar effects on the spectra of the didymium salt of strong acids were produced under conditions likely to diminish such ionisation; for example:—

(a) Addition of the sodium or potassium salt of a weak acid, such as the nitrate or acetate.

(b) The use of solvents of less ionising power than water, such as ethyl, alcohol, glycerol, &c.

(c) Combination of the didymium with a weak acid. For instance, the spectrum of didymium acetate is similar to the modified spectra produced under conditions (a) and (b), whereas that of the trichloracetate resembles exactly the ordinary spectrum of the didymium salt of a strong acid, the spectra of the mono- and dichloracetates being intermediate in character.

(d) Great concentration of the didymium salt which alters the spectrum in the same direction as addition of sodium acetate, &c.

These alterations are reversible, the ordinary spectra being restored by conditions favouring increase of ionisation of the didymium. They are not produced by non-electrolytes such as cane-sugar.

In the case of didymium acetate, mono-, di-, and trichloracetate, the change in position of the most accurately measurable line is approximately proportional to the electrical resistance.

The positions of the lines and bands in various didymium spectra were measured by photographing the modified spectrum, together with that of a standard solution of the nitrate, on the same plate, the helium lines being subsequently superposed on the whole.

*"Viscosity of Carbon Dioxide."* By P. PHILLIPS, D.Sc.

In this experiment the method of determining the viscosity is that described before this Society by A. O. Rankine in January, 1910. The viscosity of carbon dioxide is determined for temperatures of 20, 30, 32, 35, and  $40^\circ\text{C}$ . and for a range of pressures from 1 to 120 atmospheres.

When the viscosity is plotted against the pressure, the form of the isothermals is very similar to the form of the density-pressure isothermals, but the former cross whereas the latter do not. When the kinematic viscosity is plotted against the pressure it is noticed that at the saturation pressure the kinematic viscosity of the gas is the same as that of the liquid.

The minimum value of the kinematic viscosity being approximately 0.00069 at 30, 32, and at 35° C., this is taken as the critical value of the kinematic viscosity, and therefore multiplying it by the critical density, 0.464, the critical value of the coefficient of viscosity is found to be 0.000320.

When the viscosity is plotted against the square of the density it is found that, for a considerable range of density near to the critical point, the viscosity is a linear function of the square of the density. This would seem to show that the viscosity is proportional to the molecular attraction between two adjacent layers of the fluid, that is, to the  $a/\gamma^2$  term in Van der Waals' equation.

#### PHYSICAL SOCIETY.

Ordinary Meeting, May 31st, 1912.

Prof. C. H. LEES, F.R.S., Vice-President, in the Chair.

A PAPER on "*The Calibration of Wave-meters for Radio-telegraphy*," was read by Prof. G. W. O. HOWE.

Wave-meters consisting of a variable air-condenser and a set of coils can be calibrated approximately by calculation from the known capacity of the condenser and the inductance of the coils. The most probable source of error is that due to the capacity from turn to turn of the coil. This can be allowed for, with sufficient accuracy for all practical purposes, by finding the natural frequency of the coil alone, and calculating its effective or self-capacity on the assumption that the whole steady current inductance of the coil is effective even when it is oscillating freely. This capacity is then added to the capacity of the air-condenser. Another method of finding the required correction by comparison of the results obtained on the overlapping portion of the ranges of two coils is also described.

The correction can be made small by suitably designing the coils.

#### DISCUSSION.

Dr. W. E. SUMPNER remarked that it could not be considered satisfactory to find the self-capacity of a coil from its free period, taking the whole of its self-inductance as effective, until this had been shown to give the same result as that deduced experimentally with a large number of different coils.

Mr. W. DUDELL remarked that Prof. Howe's experiment showed that for practical purposes the self-capacity of a coil could be considered quite constant, for he had used much smaller external capacities than usual, and still could detect no difference. It was very important for a wave-meter to have a very definite free period of its own, and therefore  $L/R$  must be large. Its coefficient of damping should be less than that of the antenna circuit, as the usual method of finding this latter really gives the sum of the two. It was thus more important to keep the high frequency resistance of a coil small than its self-capacity. Dielectric losses were an important item in the high-frequency resistance, hence the voltage from one turn to the next should be kept down.

Prof. T. MATHER pointed out, with reference to a table Prof. Howe had put on the board, giving dimensions of different coils having the same self-induction but different self capacities, that the length of wire necessary was almost the same in each case.

Dr. W. H. ECCLES pointed out that theoretically the self-capacity could not be constant when the external capacity was small, and cited the somewhat analogous case of a weight vibrating from a heavy spring when one-

third of the weight of the spring was added to the weight provided the weight was relatively large. There might be some compensating influence at work such as the variation of the self-inductance with frequency.

Mr. A. CAMPBELL stated that the method of obtaining the working value of a wave-meter coil by finding the frequency giving resonance on open circuit was used by Dieselhorst some years ago. At the National Physical Laboratory it is customary to plot  $\gamma^2$  against the condenser capacity; over the working range the line obtained is straight, and from its slope the high frequency value of the inductance of the coil can be immediately deduced by dividing by  $4\pi^2$ . It was interesting to learn that Prof. Howe found by experiment that such a line passes through the point given by Dieselhorst's method. The capacity of a coil could be diminished by winding it in slices like the secondary of an induction coil.

The AUTHOR, in reply to Dr. Sumpner, stated that he had only experimented on three or four coils, but he had purposely used specially small added capacities in order to detect any variation of the self-capacity.

A paper on the "*Applications of Heaviside's Resistance Operators to the Theory of the Air-core Transformer and Coupled Circuits in General*" was read by Dr. W. H. ECCLES.

In circuits possessing constant inductance, resistance, and capacity the differential equations for the currents and the voltages are linear with constant coefficients, and may therefore be solved by aid of the known simple properties of symbolic operators. The symbolic operator method proves to be very compendious in problems concerning the determination of the primary and secondary currents and voltages of transformers whenever the applied E.M.F. can be expressed as an exponential function of the time, or when it consists of a sudden application of a constant or an exponential function, and also when it is impulsive.

In the paper the method is first applied to a pair of "indirectly" coupled circuits—i.e., circuits that are insulated from each other. The cases of pure magnetic coupling, pure electric coupling, and of mixed magnetic and electric coupling are treated in turn, and shown to be operationally all of the same form. Then general operational equations are obtained for direct coupling, and for mixed direct and indirect coupling—this latter, of course, includes all types of auto-transformers, both high and low frequency. Here, again, the operational equations are of the same form as in the case of magnetic coupling. The equations readily show that if the primary applied voltage be a pure sine or cosine alternating E.M.F. the well-known circle diagram for determining the instantaneous magnitudes and phases of the primary and secondary currents in an ordinary transformer is applicable to the most general type of transformer, and is capable of certain extensions. It is then shown that a similar circle diagram can be used for obtaining the primary and secondary currents in any general transformer under the application of the quasi-steady conditions of a slowly-damped alternating voltage. A further new theorem arises here, which affirms that a similar graphical method of computation can be used for deducing the voltages at the terminals of the primary and secondary condensers in a high-frequency transformer under steady or quasi-steady alternating current.

In the second section of the paper it is shown how to calculate accurately the free periods, and the damping factors of a coupled system with two degrees of freedom, and approximate formulæ are also deduced. The third section passes to the investigation of the currents and voltages produced in the circuits by sudden application or removal of a constant, a harmonic, or a damped harmonic E.M.F., and of those produced by the application of electromotive impulses. For this purpose formulæ expressing the effect of the various types of symbolic operator occurring in the paper, on impulsive E.M.F.s and on "sudden applications," are deduced and tabulated. Using these tables of integrals it is very easy to write down



quickly the solutions appropriate to any given transformer under the action of any of the types of E.M.F. specified. These tables include all the cases likely to arise in wireless telegraphy and in ordinary transformers.

As an example of the application of the methods the problem of a primary spark-circuit and its antenna is worked out under resonance conditions, and for various couplings and time graphs are made of the primary and secondary currents and voltages. A further example is the solution for the incidence of a natural electric wave (a "stray") on a receiving antenna and its resonant secondary.

#### DISCUSSION.

Dr. A. RUSSELL said that it was not quite clear how much was Heaviside's and how much was Eccles's in the first part of the paper. The latter part he considered an important piece of work.

Mr. R. APPLEYARD drew attention to a general method for the calculation of all transient phenomena, which had been worked out by Dr. H. Malcolm, described in *The Electrician* of May 10, 1912. His method is there applied to the particular case of a submarine cable, but the same general method is directly applicable to the case treated by Dr. Eccles. In the case of the telegraph cable the constants are distributed. In the case of a transformer or of any network of conductors, such as the Wheatstone bridge, the constants are localised, and the problem is easier to solve.

Some Experiments on the Movements or Semi-oily Liquids on a Water Surface were shown by Mr. CHAS. R. DARLING.

The effect produced when a drop of liquid is placed upon a clean water surface is considerably modified if the liquid be slightly soluble. Whereas a drop of oil spreads and forms a permanent film, slightly soluble liquids form films which afterwards break into globules, which if a certain minimum size be exceeded, break up into smaller globules, until a state of equilibrium is reached. The division of the films or globules is produced by indentations which spread until partition has taken place. This indentation gives to globules a reniform shape; and in certain cases the distorted globules are projected violently across the surface of the water. The effects differ in intensity with different liquids, and phenomena peculiar to a given liquid may also be noted. The following are typical examples:—

1. *Aniline*, after spreading into a film, collects into one or more large globules, which become indented round the edges, after which the globules recover their shape; the recovery, however, being accompanied by the partition of small globules. This continues until the globule is reduced to a very small size, after which no further movements are observed.

2. *Dimethylaniline* forms a film which breaks up into small globules with great rapidity. The indentations, commencing at the edges, bifurcate and spread through the film, dividing it into small parts which become globular in shape. The partition is assisted by the formation of holes in the film, from which indentations spread and meet those which commence at the edges.

3. *Quinoline* behaves similarly to (2), but the action is slower, enabling the breaking-up process to be followed easily by the eye. The small globules which are formed finally become rings, a hole appearing at the centre of each, causing the globule to spread on all sides. These rings are quite permanent, and do not appear with the other liquids mentioned.

4. *Xylidine*, 1:3:4, forms globules which become indented on one side, and then move rapidly across the surface, and then recover their shape; after which indentation and projection are repeated until the globules are broken up into smaller ones, when the action ceases. The behaviour of xylidine is similar to that of orthotoluidine, to which the author has previously called attention.

In explanation of these actions it is suggested that the surface tension of the water, which causes the drop to spread into a film, is weakened by the solution of the liquid. The opposing tensions (air-liquid and water-liquid) then overcome that of the water, with the result that the film is drawn back and indented. The strength of the air-water tension is afterwards partially restored by the sinking or diffusing of the dissolved part, so that the drawn-up mass again tends to spread. Indentations in a film or globule would therefore occur at the point at which the air-water tension had become most weakened; and if the opposing tensions were strong, the globule would be drawn across the surface. Equilibrium would then be produced when the air-water tension had become uniformly weakened, and the opposing tensions (now acting on small globules of greater curvature than the larger masses, and therefore at a larger angle to the water surface) possessed a resultant tension equal to that of the soiled water.

An account of some "Surface Leakage Experiments with Alternating Currents" was given by Mr. G. L. ADDENBROOKE.

Experiments on di-electrics at different temperatures and over a wide range of periodicity showed that the losses found were in some cases partly due to surface leakage. When this latter was eliminated and the data obtained with the surface leakage and without were compared, it did not seem as if the portion of the losses due to surface leakage could be accounted for by assuming that it was constant at all periodicities, as is the case with the losses in metallic conduction.

Measurements were therefore made to ascertain the behaviour of the surface leakage alone.

For this purpose strips of tinfoil were pasted on a sheet of glass 1 in. apart, and the relative losses with an alternating current of 42 periods and a continuous current were measured, the pressure being the same in both cases. The following are the results:—

| State of film on glass.                       | Resistance,<br>megohms. | Relative losses. |              |
|-----------------------------------------------|-------------------------|------------------|--------------|
|                                               |                         | Continuous.      | Alternating. |
| Ordinary day . . . .                          | 300                     | 1                | 3            |
| Drier day . . . .                             | 570                     | 1                | 4            |
| Film dried first in sun<br>and cooled . . . . | 770                     | 1                | 5            |
| Another glass surface . .                     | 50,000                  | 1                | 15 approx.   |

The power factor was high in all cases.

*Ebonite*.—Similar experiments showed a much higher ratio for the losses—namely, 1:40.

*Porcelain Insulators*.—The ratio in this case was as high as 1:60 on a dry day, but part of this leakage may be through the material.

The relative leakages between the primary and secondary of a small induction coil and a small transformer were respectively 1:4.5 and 1:8. In these cases also the leakage was doubtless partly through the insulation.

Further experiments described show that the moisture present must be in a very attenuated state for the differences in the losses found to become sensible. Ordinary water, even in very thin films, does not show the effect.

The striking similarity between the above results and results obtained by measurements made of these losses through dielectrics are pointed out.

The suggestion seems warranted that in both cases the effects may be due to the same fundamental cause—viz., the presence of a very diluted electrolyte.

#### DISCUSSION.

Prof. C. H. LEES pointed out that when alternating current was used there would be a capacity current flowing in the circuit as well as the surface leakage current.

Mr. A. CAMPBELL thought the results were interesting. The study of surface losses was a very difficult subject, and well deserved attention.

SOCIETY OF CHEMICAL INDUSTRY.  
(LONDON SECTION).

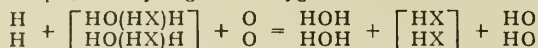
Ordinary Meeting, June 3rd, 1912.

Mr. E. GRANT HOOPER in the Chair.

THE following papers were read and discussed:—

“*Nature of the Process of Oxidation*” (With demonstrations). By H. E. ARMSTRONG and R. T. COLGATE.

The view advocated is that in all cases oxidation takes place in a system in which the oxidising agent and the oxidised substance are linked together by an electrolyte, present it may be in minute proportion but necessarily active in the process, as in the formation of water; for example, from hydrogen and oxygen:—



Hydrogen peroxide, therefore, is a necessary product of the initial process when oxygen is the oxidising agent, but may easily escape notice either because it in turn becomes the oxidising agent or because it is decomposed. According to this view the peroxides that are sometimes obtained are secondary products formed through the agency of hydrogen peroxide.

No other interpretation of the process appears to be possible if it be regarded from an electrolytic point of view—the only point of view from which chemical phenomena can be considered that has any philosophical or rational foundation.

Attention is drawn to the numerous instances in which it has been shown that hydrogen peroxide is a primary product of change when oxygen is absorbed, and to the evidence that the use of other oxidising agents is attended with the like result. Thus oxygen is evolved when either hydrogen or carbonic oxide is oxidised by permanganate (Victor Meyer).

Cases are discussed which appear to be exceptions to the rule put forward, among others those afforded by the behaviour of copper towards acids in presence of oxidising agents. Copper, it is well known, is dissolved even by weak acids in presence of gaseous oxygen, therefore it is to be expected that oxidising agents will condition the dissolution of the metal. Veley, however, has shown that hydrogen peroxide actually protects copper from dissolution by nitric acid. The conclusion this chemist has drawn that copper is dissolved only by nitrous acid, not by nitric, cannot be accepted. It is not to be expected that copper would dissolve directly in nitric acid, as its dissolution would involve an absorption of energy, but action should take place if a suitable oxidising agent were present, such as hydrogen peroxide. It is impossible to place nitric acid in a category apart from all other acids. Some explanation must be sought.

Reasons are given for supposing that in presence of certain oxidising agents the copper becomes protected by a film, presumably of peroxide.

The possible value of impurities in the copper is discussed in connection with this conclusion.

Oxidation by ozone is then considered.

“*Some Present Day Aspects of the Match Industry.*”

By E. G. CLAYTON.

White phosphorus matches and match-workers' necrosis are in Great Britain memories only. In most countries where white phosphorus matches can still be made, increasingly stringent regulations safeguard the operatives; and it may be expected that universal prohibition will eventually be reached. In the United States of America, owing to the popularity of “double-dip” matches, the tips of which contain from 14 to over 20 per cent of white phosphorus, and to climatic conditions, the conditions of work are increasingly dangerous, although serious attempts have been made to grapple with the evil; and the President of the United States recommended the discouragement of the manufacture of white phosphorus matches by the im-

position of “a heavy Federal tax.” The Diamond Match Company, owners of the letters patent for the use of phosphorus sesquisulphide in America, on January 27th, 1911, voluntarily surrendered these for cancellation, so that now any match manufacturer in the United States can freely use that compound. This will probably assist in hastening the end of the use of white phosphorus in America. There is a consensus of opinion that phosphorus sesquisulphide is free from the risks accompanying the employment of white phosphorus.

The chief match-producing countries are Sweden and Norway, America, Great Britain, Germany and Austria, China and Japan. In France the industry is a state monopoly.

There has been a gradual shrinkage in our foreign export trade.

The paper included a statement of British imports from foreign countries, particulars relating to some of the more important British and foreign match-works, an account of the modern automatic and continuous match-machinery and methods of manufacture, with an epitome of the older processes by way of contrast, references to various substances besides tetra-phosphorus trisulphide which are used, or have been suggested, as substitutes for phosphorus, and a brief description of the principal sorts of wood-stemmed, wax-stemmed, and cardboard-stemmed matches at present made.

## OBITUARY.

## M. LECOQ DE BOISBAUDRAN.

IT is with much regret that we announce the death of M. François Lecoq de Boisbaudran, which has recently taken place in the 74th year of his age.

In the special sphere to which M. Lecoq de Boisbaudran devoted himself he won great renown, and his contributions to chemical knowledge were numerous and of first-rate importance. His earliest researches dealt with the supersaturation of aqueous solutions, and the results were published in 1866. He then turned his attention more particularly to spectroscopic work, and it was in this region that his most important discoveries were made. In 1875, during the examination of the spectrum of specimens of zinc blende from the Pyrenees, he observed characteristic and hitherto unknown lines in the violet, and was hence led to the discovery of the new element gallium, the existence of which, under the name “eka-aluminium,” had already been foretold by Mendeléeff, basing his prediction upon the Periodic Table. M. Lecoq de Boisbaudran made a thorough study of his new element, describing its chemical reactions and compounds as well as its spectrum. He subsequently, in 1886, discovered the element dysprosium as one of the constituents of Soret's X, or holmium, and described its characteristic absorption spectrum. The spectroscopy of the rare earths was a subject to which he devoted much attention, and his publications included papers on terbium, gadolinium, samarium, &c. In 1885 he announced the discovery of the spectra to which he gave the name “Reversion Spectra,” and showed that spectra which are usually obtained *in vacuo* can also be obtained from solutions.

He was the author of a valuable work entitled “*Spectres Lumineux*,” which appeared in 1874. In this book the spectra of all the then known elements were described in detail and tabulated, and an Atlas of the Spectra was included. The book received a cordial welcome from workers on spectroscopy, and was looked upon as a valuable work of reference by the pioneers in this region.

M. Lecoq de Boisbaudran was a distinguished and active member of many scientific societies, and was the recipient of the Davy Medal of the Royal Society, in recognition of his valuable services to spectroscopy.



## NOTICES OF BOOKS.

*A Dictionary of Applied Chemistry.* By Sir EDWARD THORPE, C.B., LL.D., F.R.S. Volume II.; Revised and Enlarged Edition. London, New York, Bombay, and Calcutta: Longmans, Green, and Co. 1912.

The second volume of this valuable dictionary covers the letters CHI to GO. It is perhaps unnecessary to say that it is a model of accuracy and comprehensiveness, and even in the most minute details the standard set in the long and authoritative articles by chemists whose names and work are known all over the civilised world is fully maintained. The longer articles include those on Explosives, Feeding Stuffs, Fertilisers, Dyeing, Fuel, Coal, Gas, &c. The dictionary must be regarded as the standard work in the English language on applied chemistry, interpreting the word in its widest sense.

*Volumetric Analysis.* By CHARLES H. HAMPSHIRE, B.Sc. (Lond.), A.I.C. London: J. and J. Churchill. 1912.

THIS book has been written chiefly for the use of students of pharmaceutical chemistry, and gives a detailed course of volumetric analysis, covering all the work that it is desirable for them to do. The requirements of the British Pharmacopœia are specially considered, and all the methods recommended therein are included. The preparation of standard solutions is described, and the uses and advantages of the different indicators are discussed in outline. Chapters on acidimetry and alkalimetry then follow. It seems probable that it might be advisable to make some modifications in the order in which the practical work is taken up, for the early determinations are considerably more difficult and intricate than those which come later. A good chapter at the end of the book contains some miscellaneous exercises, and gives typical methods of attacking the volumetric analysis of mixtures in which the constituents to a certain extent interfere with one another's reactions.

*Lectures on Cement.* By BERTRAM BLOUNT, F.I.C. London: The Institute of Chemistry. 1912.

THE Council of the Institute of Chemistry is to be congratulated upon having arranged the special series of lectures of which these on cement are the first to be delivered. They are intended more particularly for the assistance of young chemists and advanced students, and while in no way competing with the standard text-books they will point out clearly the methods of work actually employed in practice, and will discuss the problems with which the chemist is confronted in his every-day work. These lectures are well suited to begin the series. They were delivered by one of the foremost of living authorities on cement, who presented his subject in the way that was most likely to arouse the interest and impress the minds of his audience. Assuming a knowledge of the outlines of cement making, he discussed at some length the methods of testing actually employed in practice, and went fully into the causes of failure of structures made with cement. The volume contains illustrations of the testing and sampling machines which were exhibited at the lectures.

*The History of Fire-making.* By E. BIDWELL. London: O. E. Janson and Son. 1912.

THIS illustrated catalogue contains short descriptions of the very interesting exhibit shown by the author at the Anglo-Japanese Exhibition in London in 1910. The specimens, models, &c., included many kinds of fire-drills, tinder boxes, and matches from all parts of the world, and the catalogue should prove of interest and use to collectors and museum curators.

*The Carnegie Institution of Washington.* Washington: Gibson Brothers. 1911.

THIS short record of the Carnegie Institute of Washington was issued on the tenth anniversary of its foundation. It gives some account of the general scope and plan of the Institute and short descriptions of the equipment and work of the different departments, illustrated by photographs. Taking into consideration the very short time that the great majority of the departments have been in existence, the amount of work which has been done appears very large, and speaks well for the enthusiasm of the workers and the inspiring influence of the directors.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperatures are Centigrade unless otherwise expressed.

*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. cliv., No. 18, April 29, 1912.

**Molecular Weight of Caoutchouc.**—Paul Bary.—In a mixture of sulphur and caoutchouc, suitably heated under pressure, when the quantity of sulphur combined is such that all the terminal double bonds are not saturated, the mixture contains molecules of unvulcanised caoutchouc and molecules of a sulphide of polypréne,  $(C_{10}H_{16})_nS_2$ . This substance is insoluble in benzene in the cold, while caoutchouc,  $(C_{10}H_{16})_n$ , is soluble. Thus it is easy to determine, at any rate roughly, whether any free caoutchouc is present in the mixture. The quantity of combined sulphur can be increased, until the stage is reached at which the caoutchouc is entirely insoluble in the cold. It is found that the least vulcanisation corresponds to 2.5 per cent of combined sulphur. Hence the value of  $n$  is  $\frac{97.5 \times 32 \times 2}{2.5 \times 136} = 18.4$ . Thus the molecular weight of caoutchouc at the temperature of vulcanisation ( $140^\circ C.$ ) is about  $136 \times 20 = 2720$ . At the ordinary temperature it is undoubtedly higher.

**Rôle of Valency in the Stability of Binary Metallic Combinations.**—Camille Matignon.—If  $q_1$ ,  $q_2$ , and  $q_3$  represent the heats of reaction when an atom of metal unites with hydrogen, oxygen, and nitrogen respectively, we have  $M + H_2 = MH_2 + q_1$ ,  $2M + O_2 = 2MO + 2q_2$ ,  $3M + N_2 = M_3N_2 + 3q_3$ . The stabilities of these three compounds will be comparable if the quantities  $q_1$ ,  $2q_2$ , and  $3q_3$  are of the same order of magnitude, provided, of course, that the metal and the compound remain solid at the moment of dissociation. Hence the gaseous metalloid elements form with the metals compounds of comparable stability when, in uniting with the same weight of metal, they disengage quantities of heat which are inversely proportional to their valencies.

**Preparation of Iodic Acid.**—Maurice Nicloux.—The determination of carbon monoxide by means of iodic acid, iodine being set free, gives accurate results only when the iodic acid is pure. Stas's method of preparing iodic acid is very tedious, and gives a poor yield, but the author has found that the oxidation of iodine with nitric acid presents no difficulty, and gives good yields if the nitric acid employed is of the right concentration ( $d = 1.515$  to  $1.520$ ).

**Catalysis of Cyclanols. Preparation of Cyclenes.**—J. B. Senderens.—The cyclanols can readily be dehydrated by means of sulphuric acid, cyclenes being the final products. The author has thus prepared cyclohexene and methylcyclohexenes. Menthol can similarly be converted into menthene. Potassium bisulphate and boric acid are also dehydrating catalysers for menthol, but they are much less strong than  $H_2SO_4$ . Anhydrous aluminium sulphate, which catalyses menthol very well in the dry way, gives only insignificant quantities of menthene in the wet way.

**New Classes of Oxyluminescent Compounds.**—Marcel Delépine.—The author has suggested that oxyluminescence is exhibited by organic compounds containing sulphur, in which the latter is in the half-combined state, and which, owing to the nature of the rest of the molecule, emit vapour at the ordinary temperature. Compounds in which the carbon is replaced by phosphorus, *i.e.*, the group

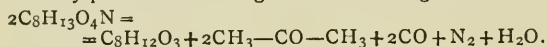
$S = C <$  by  $S = P <$  are also phosphorescent, *e.g.*,  $S = PCl_3$ .

$S = PF_3$  is very luminescent, and the active element is the sulphur and not the phosphorus, for triethyl phosphine,  $P(C_2H_5)_3$ , oxidises without luminescence in the conditions in which the sulphophosphorus compounds emit light.

**Acyclic Acid Aldehydes.**—E. Carrière.—Succinic acid aldehyde can be prepared by saponifying formyl succinic ether in aqueous solution by means of oxalic acid. When the ethereal solution is allowed to stand a polymer crystallises out. This polymer, which is a trimer, gives on distillation *in vacuo* succinic acid aldehyde and a crystalline product resulting from the condensation of two molecules of the acid aldehyde with elimination of one molecule of water. Since the etherification of the acid aldehyde gives only ether aldehyde and ether acetal, its formula must be  $CH_2=CHO$

or  $CH_2=CO_2H$ ; *i.e.*, it is a true acid aldehyde, and not an oxylactone.

**Ac-nitro Derivative of Tetramethylketofurfane.**—Georges Dupont.—When the calculated quantity of fuming nitric acid is added slowly to tetramethylketofurane and the mixture is left for some days at a temperature below  $20^\circ$   $\beta'$ -nitro- $\alpha'$ -tetramethyl- $\beta$ -ketohydrofurfane crystallises out. It is a decidedly acid compound, giving well defined salts. It is nitrated in the  $\alpha$ -position with regard to the ketone function. It is decomposed when heated at the ordinary pressure according to the following reaction:—



## MISCELLANEOUS.

**Royal Society of Arts Albert Medal.**—The Albert Medal of the Society for the current year has been awarded by the Council, with the approval of the President, H.R.H. The Duke of Connaught, to the Right Hon. Lord Strathcona and Mount Royal, G.C.M.G., G.C.V.O., LL.D., D.C.L., F.R.S., for his services in improving the railway communications, developing the resources, and promoting the commerce and industry of Canada and other parts of the British Empire.

**Meeting of Scientific and Technical Societies in Cornwall, July 16th to 20th.**—A Committee has issued an invitation to the members of Council and Officers of a number of Scientific and Technical Societies to visit Cornwall, and Mr. George T. Holloway has been asked to act as Honorary Secretary in London. Although joint meetings of Societies have been held before, this is the first time that a small representative gathering of men selected from a large number of Societies has been organised. Such meetings are generally organised on so large a scale as to almost defeat their object, but in this case the number will be limited to 100. It will include men from the Chemical Society, Institute of Metals, Institution of Civil Engineers, Institution of Electrical Engineers, Institution of Mechanical Engineers, Institution of Mining and Metallurgy, Iron and Steel Institute, and the Society of Chemical Industry. The Royal Society cannot be officially represented, as their 250th Anniversary Meeting will be held during the same week, and only a few geologists will be present, as the Geological Societies will be invited to a special meeting two years hence to celebrate the centenary of the Royal Cornwall Geological Society. The official dates are from Tuesday, July 16th,

to Saturday, the 20th, inclusive, and the programme includes visits to tin-mines, dressing floors, china-clay, engineering, and other works, and places of interest to the geologist, together with certain other functions of less scientific or technical importance but of a more social nature. Among these may be mentioned a visit to St. Michael's Mount by invitation of Lord St. Levan, and to the Royal Institution of Cornwall at Truro, and the Royal Geological Society of Cornwall at Penzance. Although the invitation is not issued directly by any of the Cornwall Societies, the Committee includes members of Council from each, and the valuable work done by the members of these Societies will receive full recognition from their *confrères* who represent the Societies which have been invited. Cornwall has reason to be proud of its Societies. They are all "Royal," and can claim both age and good work, and the names of many on the Committee which is arranging the present function are the same as were on the Committee which founded them. Such names as Davy, Watt, and a host of others, might be cited to show how important has been the work of Cornwall in the advance of both pure and applied science. The Royal Cornwall Geological Society was founded in 1814, the Royal Institution of Cornwall in 1818, and the Royal Cornwall Polytechnic Society—for which the word "polytechnic" is said to have been first coined—in 1833. The work which these Societies have done in the cause of education, and especially of mining and metallurgical education, and for geology and mineralogy, is well known. There is no mining camp or metallurgical centre where the Cornishman is not found, and the engineering profession is no less indebted to the men who were born and worked in the Duchy.

## MEETINGS FOR THE WEEK.

**MONDAY, 17th.**—Society of Chemical Industry, 8. "Production and Polymerisation of Isoprene and its Homologues," by W. H. Perkin. "A Hand Photometer," by W. J. Dibdin. "Oxidation of the Drying Oils," by J. N. Friend and W. J. Davison.

**WEDNESDAY, 19th.**—Microscopical, 8. "Notes on Pollen," by The Rt. Hon. Lord Avebury. "Demonstration of a Method of obtaining Frozen Sections after Embedding in Gelatin," by J. F. Gaskell. "On some New Astorhizidae and their Structure," by Mr. Heron-Allen and A. Earland.

**THURSDAY, 20th.**—Royal Society. "An Investigation into the Life-history of *Gladiothrix dichotoma* (Cohn)," by D. Ellis. "Relation of Secretory and Capillary Pressure—I, The Salivary Secretion," by L. Hill and M. Flack. "Origin and Destiny of Cholesterol in the Animal Organism—Part IX., Cholesterol Content of the Tissues other than Liver of Rabbits under various Diets and during Inanition," by G. W. Ellis and J. A. Gardner. "Note on the Protozoa from Sick Soils, with some Account of the Life-cycle of a Flagellate Monad," by C. H. Martin. "Variability of Streptococci in relation to certain Fermentation Tests, together with some Considerations bearing on its possible Meaning," by E. W. A. Walker. "Chemical Action on Glucose of a variety of *B. coli communis* (Escherich) obtained by Cultivation in presence of a Chloroacetate," by A. Harden and W. J. Penfold. "Action of Enzymes on Hexosephosphate," by V. J. Harding. "Oxydases of *Cytisus Adami*," by F. W. Keeble and E. F. Armstrong.

**Chemical, 8.30.** "Formation of Neon as a Product of Radio-active Change," by Sir W. Ramsay. "Colour Intensity of Copper Salts," by S. U. Pickering. "Nitrites of the Mercurialkyl- and Mercurialkylaryl-ammonium Series," by P. C. Ray, N. Dhar, and T. De. "Analysis of the Waters of the Thermal Springs of Bath," by I. Masson and Sir W. Ramsay. "Studies on certain Aliphatic Hydroxy-acids," by H. J. H. Fenton and W. A. R. Wilks. "Formation of Seven- and Eight-membered Rings from 2:2'-Ditolyl," by J. Kenner. "Studies of Dynamic Isomerism—Part XIII., Camphocarboxamide and Camphocarboxypiperidine, an illustration of Barlow and Pope's Hypothesis; Part XIV., Successive Isomeric Changes in Camphocarboxamide and Camphocarboxypiperidine," by W. H. Glover and T. M. Lowry. "Contributions to the Chemistry of the Terpenes—Part XIII., The Preparation of Pure Bornylene," by G. G. Henderson and W. Caw.



# THE CHEMICAL NEWS.

VOL. CV., No. 2743.

## THE FRUIT OF SOLOMON'S SEAL, POLYGONATUM BIFLORUM.

By ERNEST A. RAYNER.

THESE fruits grow on herbaceous plants about 3 feet in height. They are found in woods and thickets from Southern Canada, South to West Virginia, and Florida. The fruit consists of berries, which ripen during the summer months. They are pulpy, and dark blue in colour. The sample analysed was picked at Saginaw, North Carolina, in the summer of 1910.

The berries, when dried and ready for analysis, resembled huckleberries in size and appearance. The outer husk is relatively small, the main part of the berry consisting of a cluster of about ten small, round, hard, and very tough seeds.

### Analysis of the Ash.

In the following determinations we employed a modified process used in the analysis of soils and fertilisers. We made a solution of 500 cc., containing a known amount of the berries or the ash, and then used aliquot portions of this solution for the various determinations.

We first prepared the solution by digesting 10 grms. of the berries with strong hydrochloric acid, and then attempted to destroy the organic matter with nitric acid. But we could not eliminate all of the organic matter, and that which remained interfered with subsequent precipitations.

We then ashed exactly 10 grms. of the fruit, and digested the ash in strong hydrochloric acid. This method was successful. The insoluble residue was filtered off for the silica determination, and the filtrate made up to 500 cc., which we will call Solution I. Each 100 cc. portion contains the ash of 2 grms. of the fruit, and the work of making the numerous determinations is greatly lessened.

We took 100 cc. of Solution I., and precipitated the iron and alumina, separated these, and weighed them as oxides. The calcium was precipitated in the filtrate as oxalate, and we found no magnesia.

Secondly, from another 100 cc. portion of Solution I. we determined the alkalis by evaporating nearly to dryness, and changing the chlorides to sulphates by heating with strong sulphuric acid. The sulphates were dissolved in a little hot water, filtered into a large porcelain crucible, a little hydrochloric acid was added, and the determination of the alkalis continued by the J. Lawrence Smith method.

Thirdly, we used another 100 cc. portion for the determination of the phosphate. The solution was warmed, carefully neutralised with ammonia, and we cleared the solution with nitric acid. After adding some ammonium nitrate, the solution was heated, ammonium molybdate solution was added, and the usual methods followed for the estimation of  $P_2O_5$ .

In the fourth 100 cc. portion of Solution I. we determined the sulphate with barium chloride in the usual way. Careful tests were made for manganese and chromium, but neither seemed to be present.

The analysis resulted as follows:—

|                                        | Per cent of the ash. |
|----------------------------------------|----------------------|
| SiO <sub>2</sub> .. .. .               | 0.80                 |
| Fe <sub>2</sub> O <sub>3</sub> .. .. . | 13.65                |
| Al <sub>2</sub> O <sub>3</sub> .. .. . | 14.75                |
| CaO .. .. .                            | 4.60                 |
| MgO .. .. .                            | —                    |
| K <sub>2</sub> O .. .. .               | 24.19                |
| Na <sub>2</sub> O .. .. .              | 17.25                |
| P <sub>2</sub> O <sub>5</sub> .. .. .  | 24.58                |
| SO <sub>3</sub> .. .. .                | 0.44                 |
|                                        | 100.26               |

It occurred to us it might be interesting to note the difference in the composition of the ash of the outer husk and the seeds. We therefore made an analysis of the ash of the husk, and calculated that of the seeds by difference. The husks were easily removed. The ash analysed as follows:—

|                                        | Per cent of the ash. |
|----------------------------------------|----------------------|
| SiO <sub>2</sub> .. .. .               | 0.76                 |
| Fe <sub>2</sub> O <sub>3</sub> .. .. . | 13.95                |
| Al <sub>2</sub> O <sub>3</sub> .. .. . | —                    |
| CaO .. .. .                            | 4.78                 |
| MgO .. .. .                            | —                    |
| K <sub>2</sub> O .. .. .               | 55.87                |
| Na <sub>2</sub> O .. .. .              | 0.15                 |
| P <sub>2</sub> O <sub>5</sub> .. .. .  | 24.62                |
| SO <sub>3</sub> .. .. .                | —                    |
| Total .. .. .                          | 100.13               |

A comparison of the two results shows that the difference is mainly a loss of 14.75 per cent Al<sub>2</sub>O<sub>3</sub> in the husk and 17.25 per cent Na<sub>2</sub>O. The other differences are slight, and may be due to experimental errors in working with such small quantities.

The ash of the 10 grms. of original fruit weighed 0.2270 grms., or 2.27 per cent.

### The Sugars.

We treated 200 grms. of the fruit one month with 95 per cent alcohol. A fresh portion of alcohol was added each day during the first two weeks and on alternate days during the remainder of the time. A week's treatment with hot water removed the last trace of sugar. The alcoholic and water extractions were determined separately with Fehling's solution, 10 cc. of which corresponded to 0.05 gm. sugar. The alcoholic extraction gave 11 per cent by weight of the berries and the water extraction 1.48 per cent, a total of 12.48 per cent.

A portion of the combined alcohol and water extractions was treated with bone-black, a dark brown syrup was obtained, upon which further treatment with bone-black had no effect. We then made Mulliken's test ("Allen's Commercial Organic Analysis") with phenylhydrazine hydrochloride. A slight osazone precipitate appeared in one and a-half minutes, which attained a maximum in four minutes. The test indicates that the sugar is mainly glucose with a small quantity of fructose.

We tested further with a 3 per cent solution of caustic soda ("Allen's Commercial Organic Analysis"), and obtained the deep brown colour characteristic of dextrose.

There was on hand in the laboratory a quantity of the fruits obtained the previous year, which had become mouldy before they could be dried. We determined the sugar in these, and found only 1.07 per cent. The tests showed only a trace of fructose and the main portion glucose.

### The Oil.

The residue from the sugar extraction was thoroughly dried and treated with ether to extract the oil. The seeds were broken up in a coffee mill as fine as possible, but they were hard and tough and could not be reduced to a fine powder. The unusually long time of three hundred and fifty hours treatment with ether was required to extract all the oil. After purifying and drying, the oil weighed 10 grms., or 2 per cent of the original fruit. It was transparent, yellowish green, with an odour and taste resembling castor-oil. The specific gravity was 0.9444, that of castor-oil being 0.9599 at 16°.

A portion of the oil weighing 2.0382 grms. was saponified with difficulty after heating a considerable time. The saponification equivalent by Koestorfer's method was 327, which furnished additional evidence that it was castor-oil, whose saponification equivalent is 319—326.

The contents of the flask after the saponification were shaken with ether. When the ether was removed by distillation there remained the unsaponifiable portion

which is doubtless a glyceride present with the oil. The neutral solution in the flask was acidified with hydrochloric acid, and two portions or acids separated out; a light oily substance which collected at the top, and a whitish heavier substance appeared on the bottom. The oily substance was doubtless ricinolic acid, but both were present in such small quantities that no further treatment of them was attempted.

#### Nitrogen.

A separate portion of the berries was weighed out for the determination of nitrogen. The Kjeldahl method was used. The amount found was 1·88 per cent of the dried fruit.

When grinding the berries an odour strongly resembling tobacco was very noticeable. We made several attempts, but failed to get any test for nicotine or conine.

#### Summary of Results.

|                                          | Per cent. |
|------------------------------------------|-----------|
| Ash .. .. .                              | 2·27      |
| Sugar .. .. .                            | 12·48     |
| Nitrogen .. .. .                         | 1·88      |
| Oil .. .. .                              | 2·00      |
| Other substances, cellular tissue, water | 81·37     |
|                                          | 100·00    |

I gladly take this opportunity of expressing my gratitude to Dr. N. Knight for his assistance in this work.

Cornell College, June 1, 1912.

#### ON THE TRANSPORT OF MUD BY A RIVER IN FLOOD.\*

By THOS. STEEL, F.L.S.

DURING an unusually heavy flood which occurred on the River Yarra, Victoria, in the month of July, 1891, I took the opportunity of making a daily examination of the amount of suspended mud carried by the water. The samples were drawn from the river at the Sugar Refinery, Yarraville, at a point just above the junction of the Goode Canal with the river, and hence include the flood waters of the Saltwater River and those of the Yarra itself, except what escaped by the Goode Canal. In normal times at Yarraville, and for some distance further up, the river is tidal, and its water contains a large proportion of sea-water. The suspended mud was coagulated by the addition of a minute quantity of alum to a measured volume of the water; allowed to settle, the clear water decanted, and the mud collected on a tared filter, dried in the water-bath, and weighed. The dry mud was then ignited, and the loss in weight noted. During part of the period of observation the chlorine in the water was determined as an index of the amount of sea-water working up the River from Hobson's Bay.

The accompanying table shows the results of the observations. The quantities are stated in parts per 100,000 water.

It is interesting to note how with the recurrence of rain a second flood was in evidence on August 3rd and 4th, which brought down on one day considerably more mud than on the heaviest day of the primary flood. Doubtless this was due to the washing down of mud which had been freshly deposited on the river banks, and was disturbed again by the rising waters.

The Chief Engineer for Water Supply, Mr. Stuart Murray, kindly furnished me at the time with the official departmental estimate of the quantity of water flowing past the spot where the samples were taken, during the period from July 10th to 22nd inclusive, this being 14,000,000,000 cubic feet. I was unable to ascertain the daily flow, but

| 1891.   | Total mud. | Mud after ignition. | Chlorine. | Equivalent percentage sea-water. | State of river. |
|---------|------------|---------------------|-----------|----------------------------------|-----------------|
| July 10 | 101·85     | 96·50               | —         | —                                | High—rising.    |
| " 13    | 171·80     | 153·65              | —         | —                                | Highest.        |
| " 14    | 81·65      | 73·85               | —         | —                                | High—falling.   |
| " 15    | 48·85      | 42·95               | —         | —                                | High—falling.   |
| " 16    | 25·75      | 22·05               | —         | —                                | Falling.        |
| " 17    | 16·40      | 13·75               | —         | —                                | Almost level.   |
| " 18    | 11·20      | 9·60                | —         | —                                | About level.    |
| " 20    | 10·80      | 8·90                | 63·1      | 3·5                              | About level.    |
| " 21    | 11·55      | 9·50                | 120·7     | 6·8                              | Level.          |
| " 24    | 12·45      | 9·40                | 142·0     | 8·0                              | Level.          |
| " 29    | 13·70      | 10·50               | 166·9     | 9·4                              | Level.          |
| Aug. 3  | 290·80     | 263·80              | 6·4       | 0·4                              | Strong fresh.   |
| " 4     | 147·05     | 133·25              | 2·8       | 0·16                             | Falling.        |
| " 5     | 65·80      | 58·15               | 4·3       | 0·24                             | Level.          |
| " 6     | 31·05      | 26·50               | 43·4      | 2·4                              | Level.          |
| " 7     | 24·40      | 20·75               | 72·9      | 4·1                              | Level.          |
| " 8     | 20·90      | 17·65               | 74·7      | 4·2                              | Level.          |

taking the mean figures July 10th to 21st, as given in the table, the amount of mud carried by the water would be about 53·32 parts per 100,000. This gives a total of about 207,000 tons dry mud transported by the water during the period mentioned.

Much of this load of mud was deposited in the bay, near the mouth of the Yarra, forming a huge bank extending towards St. Kilda. While the river bed was pretty completely scoured clear of mud, leaving the hard bottom, it was estimated that the entrance was silted up at least two feet, and several steamers ran aground while endeavouring to enter the river.

The late Prof. Kernot contributed a paper descriptive of this flood, and detailing the methods to be carried out to prevent a recurrence, to the Royal Society of Victoria (*Proc. Roy. Soc. Vict.*, 1892, Part II., N.S., iv., 209; observations were also made by W. W. Culcheth, *Proc. Vict. Inst. Eng.*, 1891).

I have to acknowledge the assistance of Messrs. H. L. Whitaker and W. E. Appleby in the determination of the amounts of mud in the water.

With regard to the composition of the mud brought down by flood waters, an analysis of a sample deposited on the banks of the Tweed River, New South Wales, by a flood in November, 1882, which I examined at the time, will be of interest. The mud formed a coating varying up to one inch in thickness on the river banks, and on drying cracked into flat biscuit-like pieces. The analysis was made by boiling with hydrochloric acid, the solution being dealt with in the usual manner.

#### Sample Dried at 110° C.

|                               |       |
|-------------------------------|-------|
| Organic matter, &c. (a) .. .. | 22·47 |
| Sand and insoluble .. .. .    | 55·38 |
| Soluble silica .. .. .        | 0·31  |
| Ferric oxide .. .. .          | 5·51  |
| Ferrous oxide .. .. .         | 1·73  |
| Alumina .. .. .               | 10·78 |
| Lime .. .. .                  | 1·16  |
| Magnesia .. .. .              | 0·71  |
| Potash .. .. .                | 0·20  |
| Soda .. .. .                  | 0·07  |
| Sulphuric anhydride .. .. .   | 0·67  |
| Phosphoric oxide .. .. .      | 0·36  |
| Carbon dioxide .. .. .        | 0·13  |
| Chlorine .. .. .              | 0·03  |
| Not determined and loss .. .. | 0·50  |

100·01

Oxygen equivalent to chlorine .. 0·01

100·00

(a) Containing nitrogen, 0·48. Water in air-dried sample, 5·84.

\* A Paper read before the Australasian Association for the Advancement of Science, April 3, 1912.



# A MEASUREMENT OF THE TRANSLUCENCY OF PAPERS.\*

By C. FRANK SAMMET,  
Assistant Chemist, Leather and Paper Laboratory.

THAT property of paper which permits light to pass through it is usually spoken of as its transparency. Although this term can not be concisely defined, it more commonly refers to the transmission of the greater portion of incident light through matter without scattering. Paper is of such a discontinuous nature that light in transmission is always more or less scattered. This characteristic is more definitely expressed by the word "translucency," which is, therefore, to be preferred to "transparency." "Opacity," the inability to transmit light, can not properly be used to express the degree of translucency or transparency of paper.

Translucency is quite an important property of paper, especially of printing, envelope, parchment, and so-called transparent papers. The first two classes should not be so translucent that printing or writing will show through sufficiently either to inconvenience or to tire the eye, while the latter kinds should be so nearly transparent that characters may be easily and quickly read through them. Many procedures have been suggested for the measurement of translucency, but few of them have proved to be of any practical significance, and, as a rule, they have given only comparatively results. A numerical expression is desired which will be standard in the valuation of the translucency of papers as established by the normal eye.

The most satisfactory instrument heretofore proposed for this measurement is the grease-spot photometer (*Wochenblatt für Papierfabrikation*, 1910, xli., 4404; *Papier Zeitung*, 1908, No. 50; Klemm, *Handbuch der Papierkunde*, 2. aufl., p. 323—325). This consists of two lights of equal intensity with a spot screen equidistant between them. The paper to be examined is placed between the screen and one of the lights. The latter is moved until the light falling upon the screen is the same from both sides. The ratio of the distances of the lights from the screen is an expression of the translucency of the paper (Böhm's method).

The instrument devised by Klemm, in which successive sheets of the paper are inserted until the light from a 1-candlepower Hefner burner is cut off, is totally unsuitable to express the translucency of paper when it is looked at rather than through. Serious inaccuracies arise with this instrument due to differences in surface, colour in the paper, the transmission of light through more than one sheet and across intervening air spaces, and the retention of colour sense by the eye, any one of which produces wide variations and in some instances a reversal of the sequence of translucency. It also gives inaccurate results on coloured papers, and, furthermore, it measures the light transmitted through the paper once, while ordinarily that which has been transmitted to the eye after reflection from a surface underneath is the light which it is desired to measure.

The procedure to be described is free from the foregoing objections, and for practical purposes determines any degree of translucency, in white as well as coloured papers, in terms of a standard. When a paper is placed over a white surface the luminosity observed is composed of the light reflected from the surface of the paper plus that which is reflected from the surface underneath. When the paper is placed on a perfectly black surface the luminosity is that of the light reflected from the surface of the paper only as the transmitted light has been absorbed. The difference of the values which measure these two effects gives an expression for the light transmitted, and therefore for the translucency of the paper. These measurements may be obtained by means of the tint photometer, which is constructed and operated as follows:—

Two blocks of magnesium carbonate are used as a standard white background. A piece of black velvet is most satisfactory as a black or absorbing background. The rays of the sun diffused through tracing cloth or white paper evenly illuminate the white surfaces of the blocks. These are viewed in a mirror on reflection through two apertures, which are focused by a specially ground lens into semicircular fields. One aperture is controlled by a shutter operated by a lever that reads 100 when wide open and zero when closed on a scale divided into millimetres, whereby any degree of luminosity may be obtained. In order to counteract the confusing impression different kinds of surfaces may have on the eye, the light is passed through a series of revolving lenses, thus producing uniform fields. It would be rather difficult to match the luminosity of fields of different tints, and to eliminate this effect the fields are viewed through a coloured glass of some primary colour. The luminosity observed is inappreciably affected thereby in the case of white papers, and the same is true with those of deep tints, if the measurements are made through a glass of the primary colour representative of the predominating hue of the paper. Red, green, and blue glasses have proved satisfactory.

After the fields are matched the black velvet background is placed over one block. The paper whose transparency is to be determined is then placed over both blocks. By operating the shutter the luminosity of the lighter field (due to the light reflected from the surface of the paper plus the transmitted light reflected from the surface of the block underneath) is reduced until it matches that of the field with the black velvet background, the luminosity of which is due to the light reflected from the surface of the paper only, as the transmitted light has been absorbed. Hence the value of the lowering of the reading (100—the reading observed) is a measure of the transmitted light reflected from the surface underneath, i.e., of the translucency of the paper. Care should be taken to match the fields before a reading is taken. The paper should be in immediate contact with the background. The coloured glass used in the reading should be as near a pure primary colour as possible. Check results can be obtained within one division of the scale.

## Determinations (loc. cit.) of the Translucency of Papers by Two Methods.

| Kind of paper.               | Order according to normal eye. | Proposed method (100—reading). | Photometer method of Böhm (loc. cit.) calculated by formula $(t-b)/(a^2) \times 100$ |
|------------------------------|--------------------------------|--------------------------------|--------------------------------------------------------------------------------------|
| Japanese press copy (white)  | 1                              | 66                             | 34.5                                                                                 |
| Parchment (cream) .. ..      | 2                              | 58                             | 33.5                                                                                 |
| Press copy (brown) .. ..     | 3                              | 55                             | 49.5                                                                                 |
| Glazed onionskin (white) ..  | 4                              | 40                             | 54.5                                                                                 |
| Typewriter (white) .. ..     | 5                              | 37                             | 60.0                                                                                 |
| Bond (pink) .. ..            | 6                              | 32                             | 65.5                                                                                 |
| Typewriter (white) .. ..     | 7                              | 28                             | 64.5                                                                                 |
| Bond (orange) .. ..          | 8                              | 27                             | 67.5                                                                                 |
| Filter (white) .. ..         | 9                              | 25                             | 65.5                                                                                 |
| Bond (yellow) .. ..          | 10                             | 20                             | 68.0                                                                                 |
| Bible (cream) .. ..          | 11                             | 18                             | 68.0                                                                                 |
| Ledger (white) .. ..         | 12                             | 18                             | 69.0                                                                                 |
| " .. ..                      | 13                             | 17                             | 70.0                                                                                 |
| Writing, linen finish (blue) | 14                             | 16                             | 68.0                                                                                 |
| Laid envelope (white) ..     | 15                             | 14                             | 69.5                                                                                 |
| Scratch pad (white) .. ..    | 16                             | 2                              | 79.5                                                                                 |

The proposed method gives more satisfactory results than those previously suggested, especially in the case of coloured papers, and is perhaps more convenient in manipulation. The result gives the translucency usually sought, namely, the transmission of light through the paper and reflection from the surface underneath, while the other photometer methods indicate the direct transmission. No errors of sufficient magnitude to interfere with the sequence of translucency as established by the

\* Circular 96, United States Department of Agriculture, Bureau of Chemistry.

normal eye have been observed. The figures in the second column express the translucency of the paper as determined by the proposed procedure. They also express directly the percentage of incident light transmitted through the paper and reflected back through it by the standard white surface upon which it rests. The results obtained by the proposed method and by the Böhm method are given in the table. The readings are on papers which range, to the normal eye, from very translucent to almost opaque.

## THE PREPARATION AND PROPERTIES OF METALLIC CERIUM.\*

By ALCAN HIRSCH.

(Continued from p. 281).

### *Electrolysis of the Anhydrous Fluorides.*

WHEN it was found that the electrolysis of the chlorides was such a difficult process, it was thought that the electrolysis of some other salt might be more easily effected. Muthmann (Muthmann, Weiss, and Schiedmandel, *Liebig's Annalen*, 1907, ccclv., 116—136) has used the solution of the oxides in the fused fluorides, similar to the process for the production of aluminium.

The anhydrous mixed fluorides melt at a temperature of a little over  $900^{\circ}$ , and dissolve the mixed oxides with avidity. The electrical conductivity of the molten fluorides is low, but increases rapidly with addition of oxides. The solution containing about 20 per cent of oxides conducts very well.

The first cell tried with the fluorides contained a graphite cathode insulated from the graphite vessel by a porcelain ring. During the electrolysis the porcelain was badly attacked by the fused fluorides. Even a Dixon crucible was badly eroded, as the fluorides attacked the silicate binder. It was found that graphite was one of the few substances that would withstand the high temperature and the action of the fused fluorides. A vessel made of graphite plates, luted on the edge with graphite-molasses paste, clamped together with iron bands, and previously baked, leaked during the electrolysis. Although the vessel was embedded in magnesia flour to prevent oxidation, the high temperature of the bath (well over  $1000^{\circ}$ ) caused the luting to break down.

A summary of the results of the runs using fluoride-oxide electrolyte are here given.

1. 2500 grms. anhydrous mixed fluorides were melted in a resister furnace. The fused fluorides readily dissolved 450 grms. of mixed oxides. The molten bath was electrolysed, using 450 ampères at a pressure of 14 volts. 10—15 grms. of impure metal were obtained. The electrolysis was unsatisfactory, as the anode was not properly "wet" by the electrolyte. The active surface of the anode should have been much greater. A layer of carbide was found on the bottom and sides of the crucible.

2. A graphite box, inside dimensions  $4\frac{1}{2} \times 5 \times 6$  inches ( $11 \times 12 \times 15$  cm.), which was chiselled from a solid graphite block, was used as the electrolytic vessel. The anode was made as follows:—A graphite block about 16 ins. (40 cm.) long, 3 ins. (8 cm.) wide, and 2 ins. (5 cm.) thick was cut at one end so as to present three blades, each  $\frac{1}{2}$  in. (1 cm.) thick and 3 ins. (8 cm.) wide. This increased the active surface of the anode and resulted in its functioning properly. The fluorides were melted by a carbon heater placed between the electrodes. As soon as a small amount of the fluorides was melted, the heater was removed, the anode lowered, and alternating current turned on. 1000 ampères at 24 volts for about twenty-five minutes were required to melt 4300 grms. mixed fluorides. Mixed

oxides were added gradually, and then direct current switched on. 650—750 ampères at a pressure of 10 volts were used. Oxide was added gradually during the course of the run, which was continued for about an hour, at the end of which time the solution solidified. 4300 grms. fluoride and 1600 grms. oxide were used in all. Small amounts of metal were scattered throughout the mass, but no regulus was obtained. At the bottom of the vessel was found a black layer of carbide. The melting-point of the fluoride-oxide mixture was about  $1400^{\circ}$ .

The principal difficulties encountered in the electrolysis of the oxides dissolved in the fused fluorides were:—

1. Oxides must be added to the fluoride to make a sufficiently conductive solution, and the melting-point of the bath is very high.

2. At the high temperature of the bath, rare-earth metal and graphite combine to form carbide.

Attempts were made to electrolyse a solution of the oxides dissolved in a mixture of fused potassium fluoride and rare-earth fluorides. Violent explosions ejected a large portion of the electrolyte during the run, due perhaps to the deposition of alkali metal, which was immediately vaporised at the temperature of the bath.

One of the principal difficulties in all the previous electrolyses had been the formation of carbides, which made the bath viscous and unfit for electrolysis. It was thought that if a non carbon cell was used the formation of carbide would be less likely to occur, as the only carbon in the cell would be the anode. On account of their corrosive action and high melting-point the fluorides could not well be used in other than carbon vessels. It was therefore decided to try the electrolysis of the mixed chlorides in a wrought-iron vessel (kindly suggested by Dr. W. H. Walker, of the Mass. Inst. Tech.).

### *Later Work on the Electrolysis of the Anhydrous Chlorides.*

1. The electrolytic vessel was a thin-walled wrought-iron crucible about 3 ins. (8 cm.) high and 2 ins. (5 cm.) average diameter. The anhydrous mixed chlorides were fused by means of a thin carbon rod, heated electrically to incandescence, and electrolysed with a current of about 50 ampères for several hours. The electrolyte remained fluid during the entire course of the electrolysis. About 30 grms. of semi-fused metal were obtained.

The iron crucible was not attacked. The success of this run led to experiments on the best conditions for electrolysis on a larger scale.

2. The electrolytic vessel was a large iron crucible  $5\frac{1}{2}$  ins. (14 cm.) maximum inside diameter and 7 ins. (18 cm.) high. The anode was a carbon rod  $1\frac{1}{2}$  ins. (4 cm.) in diameter. A small amount of sodium chloride was fused, and the mixed chlorides were added in small amounts until a fused bath was obtained. The electrolysis was maintained with a current of 130 ampères for four hours at a pressure of 12—18 volts. Small amounts of anhydrous potassium fluoride (about 10 grms. at a time) were added occasionally to dissolve what little oxide was formed and so keep the bath perfectly fluid. The amount of additional salts used (KF plus NaCl) in all was about 10 per cent by weight of the rare-earth chlorides. A lump of partially fused metal was obtained, which when re-melted under NaCl weighed 120 grms. The number of ampère hours used was 520, and the ampère efficiency was  $13\frac{1}{2}$  per cent. The crucible was not attacked.

3. The object of this run was to try the value of an insulated cathode. Previous experience had taught that if the insulated cathode was iron and a fairly large current used (about 200 ampères) the iron cathode would become so hot that an alloy would be produced. Consequently iron was not used as the cathode in this electrolysis. The electrolytic vessel consisted of a 6-in. (15 cm.) length of a 3-in. (8 cm.) iron pipe screwed into a reducing-cap carrying a short piece of 2-in. (5 cm.) pipe. The cathode consisted of a long rod  $1\frac{1}{2}$  in. (4 cm.) graphite insulated from the sides of the 2-in. (5 cm.) pipe by asbestos fibre, and encased at the bottom in plaster of Paris. A sketch of

\* A Paper presented at the Twentieth General Meeting of the American Electrochemical Society, Toronto, Canada, September 1911. From the *Journal of Industrial and Engineering Chemistry* ii., No. 12.



this cell is shown in Fig. 6. The anode was a graphite rod  $1\frac{1}{2}$  in. (4 cm.) in diameter. A current varying from 180 to 200 amperes at a pressure of 20 volts was used for nearly four hours. A regulus of metal weighing 135 grms. was found at the bottom of the vessel. Below the metal was a black layer of carbide. The number of ampère hours was 712, and the ampère efficiency was 11 per cent. The electrolyte consisted of the mixed chlorides, to which were added, during the course of the run, small amounts of anhydrous potassium fluoride, sodium chloride, and barium chloride. The object of the last-named salt was to increase the resistance of the bath so that the electrolyte was kept well fused and metallic conduction of the bath prevented. It must be remembered that where a graphite anode was used, a higher voltage was required to keep the bath fused.

The results of the above three experiments showed:—  
(1) That rare-earth metal could be produced by electrolysis of the chlorides in iron vessels; (2) that the use of an insulated cathode of graphite gave a lower current efficiency and resulted in some of the metal being converted to carbide; (3) that it was necessary to regulate

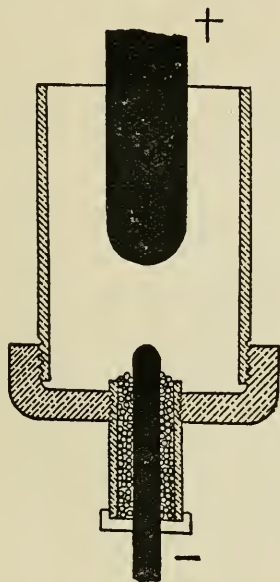


Fig. 6.

the temperature of the bath so as to have the electrolyte well fused and yet well below the alloying temperature of iron and rare-earth metal; and (4) that control of the electrolysis could be maintained by judicious addition of small amounts of potassium fluoride, sodium chloride, and barium chloride.

The above experiments in which the anhydrous mixed chlorides were used were so successful that the method of electrolysis was applied to pure anhydrous cerous chloride, and the runs are here described.

1. The electrolytic vessel was a thin-walled wrought-iron crucible, maximum diameter about 4 inches. The anode was a round graphite electrode 1 inch in diameter, and the iron crucible was made the cathode. A small amount of sodium potassium chloride was first melted, and then cerous chloride added. During the course of the electrolysis, rather large amounts of the alkali chlorides were used. A current of 110 amperes was employed for two hours, at the end of which time the electrolyte solidified. Forty grms. of fairly well-fused metal was obtained. The number of ampère hours was 220, and the ampère efficiency was 11 per cent. Too much alkali chlorides was added during the electrolysis, and this fact,

together with the high temperature of the bath, accounts for the efficiency. (In many electrolyses a high ampère efficiency is obtained only if the bath is kept near its melting-point. As the temperature is raised the efficiency decreases. This is especially true in the case of fused lead chloride and fused caustic soda, where if the temperature of the bath is high, no metal at all is obtained. See these *Trans.*, 1911, xix., 167–168; Discussion).

2. A crucible similar to the one described in the above experiment was used both as the containing vessel and cathode. A corrugated graphite anode  $\frac{1}{2}$  in. (1.6 cm.) in diameter was used. 250–300 grms. of anhydrous cerium chloride and about 10 per cent sodium chloride were used. The electrolysis was continued for one and a-half hours, using 75 amperes at 15 volts. The bath was kept near its melting-point, so that there was no danger of a cerium-iron alloy forming. Sixty-five grms. of cerium metal were obtained. The number of ampère hours was 112, and the ampère efficiency was 33 per cent.

3. It was decided to try the electrolysis on a larger scale. When the mixed rare-earth chlorides were electrolysed in a large iron crucible, it was difficult to remove the solidified salt after the run was completed. The chlorides, after cooling, form a hard vitreous mass, upon which even a cold chisel has little effect. The removal of slag and metal was always accomplished with difficulty and loss of some material. To obviate this difficulty a 7-in. (18 cm.) length of a 3-in. (8 cm.) iron pipe, screwed into a cap for a bottom, was used as the electrolysing vessel (see Fig. 7).

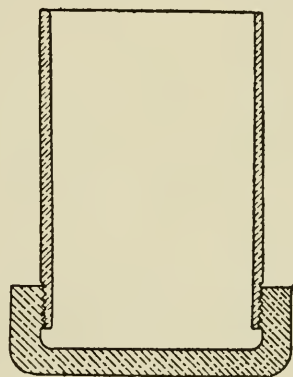


Fig. 7.

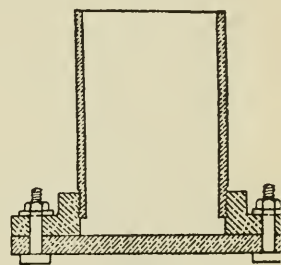


Fig. 8.

Sodium chloride was melted first, and cerous chloride added until the fused mixture conducted well, when the carbon electrode,  $1\frac{1}{2}$  in. (3 cm.) in diameter, was lowered until it was within an inch or so of the bottom; the voltage then sank to the proper value, 12 volts, and electrolysis began. The volume of the bath, of course, constantly decreases during the electrolysis, and fresh cerous chloride must be added from time to time. About every forty minutes the anode was raised until it just dipped below the surface of the bath. This increased the voltage across the bath and caused a rapid heating of the electrolyte. After a few minutes the anode was lowered until the voltage was properly adjusted, when electrolysis recommenced. The voltage varied from 12 to 14 volts, and the average current used was 200 amperes, for four hours. The electrolyte became slightly viscous toward the end of the run, but the electrolysis proceeded satisfactorily, as was indicated by the appearance of the bath, the voltage across the cell, and the evolution of chlorine. Over a kilogram. of cerous chloride was used. A well fused ingot of metal weighing 580 grms. was obtained. The number of ampère hours was 800, and the ampère efficiency was  $4\frac{1}{2}$  per cent. The cap could not be removed at the completion of the electrolysis, but the crucible was unattacked by the cerium. The small amount of iron intro-

duced was caused by oxidation of the heated vessel near the top, the solution of this iron oxide in the electrolyte and its immediate reduction to metal when in contact with cerium.

4. In order to facilitate the removal of electrolyte and metal at the end of a run, the following vessel was devised:—It consisted of a 3-in. (8 cm.) iron pipe screwed tightly into a 5-in. (13 cm.) iron flange, to which a bottom plate was attached by means of four large bolts and nuts (see Fig. 8). The electrolyte was cerous chloride containing a small percentage of sodium chloride, to which very small amounts of potassium fluoride and potassium fluoride-barium chloride mixture were added when required (about every half hour or so). The function of these additional salts has already been explained in detail. The voltage was kept at its proper value, which should not be greater than 15 volts. The average current used was 200 amperes for three hours. The electrolysis required attention about every twenty minutes; that is, the anode needed slight adjusting or the temperature had to be corrected. An ingot weighing 380 grms. was obtained. The number of ampere hours was 600, and the ampere efficiency 36.5 per cent.

The electrolyte remained liquid during the entire course of the electrolysis. About 1½ kilogrms. of cerous chloride were used. The cell held perfectly, and at the end of the run the electrolyte and metal were easily removed. This type of electrolytic vessel is highly recommended for similar work. Care should be taken that the flange and bottom plate are well faced and that the lap is wide enough—at least 1½ in. (4 cm.).

#### Analysis of Cerium and "Mischmetall."

Two methods of analysis were used in this research for the determination of cerium:—

1. *Gravimetric.*—The cerium group was separated from all the other metals by precipitation of the oxalates in faintly acid chloride or nitrate solution by means of boiling oxalic acid. Calcination of the oxalates at blast lamp temperature gave the oxides (in the case of cerium the dioxide  $\text{CeO}_2$ ), which were weighed.

2. *Volumetric.*—A modification of Browning's method was used (*Am. Journ. Sci.*, 1899, [8], xlviii., 451; *CHEM. NEWS*, lxxxi., 30, 41; Browning and Palmer, *Am. Journ. Sci.*, 1908, xxvi.). It depends upon the oxidation of cerous salt to ceric, in alkaline solution, by means of potassium ferricyanide. Browning determined the excess of ferricyanide.

The modification was as follows:—A slight excess of a dilute solution of potassium ferricyanide was added to the solution of cerous salt, and KOH added. This precipitation was usually done in a bottle, which was afterwards centrifuged. The supernatant liquid was decanted through a small Gooch filter to guard against any loss of precipitate. The ceric hydroxide was washed two or three times with hot concentrated KOH to remove the ferro- and ferricyanides centrifuging after each washing. The ceric hydroxide was then treated with potassium iodide solution, whereby the cerium is reduced to the cerous state and free iodine liberated, which latter is determined by titration with thiosulphate. By this method cerium may be determined in the presence of thorium and the other members of the cerium group. This method is accurate to one-half per cent.

| Grms. cerium present.                                   | Grms. cerium found. | Error. Grm. | Error. Per cent. |
|---------------------------------------------------------|---------------------|-------------|------------------|
| 0.22648 .. ..                                           | 0.22697             | 0.00049     | +0.2             |
| 0.22648 .. ..                                           | 0.22657             | 0.00009     | +0.04            |
| 0.22648 .. ..                                           | 0.22697             | 0.00049     | +0.2             |
| 0.22648 .. ..                                           | 0.22752             | 0.00214     | +0.5             |
| 0.22648 Ce ..                                           | 0.22737             | 0.00089     | +0.4             |
| 0.4 Th( $\text{NO}_3$ ) <sub>4</sub> ..                 | —                   | —           | —                |
| 0.11328 Ce ..                                           | 0.11388             | 0.00060     | +0.5             |
| 0.10 La <sub>2</sub> (SO <sub>4</sub> ) <sub>3</sub> .. | —                   | —           | —                |

Analysis of a sample of "mischmetall" by the volumetric method showed a cerium content of 70.5 per cent.

Analysis of metallic cerium prepared in Run 1, above, showed the following composition:—

| Per cent cerium. | Per cent iron. |
|------------------|----------------|
| 97.5             | 1.2            |
| 97.8             | —              |
| 97.8             | —              |

The determination of cerium by the gravimetric method in the cerium metal prepared in Run 4, above, showed 97.8 per cent cerium.

Analysis of cerium cast into rods in an iron mould was as follows:—

|                              | Per cent. |
|------------------------------|-----------|
| Cerium .. .. .               | 93.6      |
| Iron .... .                  | 4.5       |
| Insol. residue (oxide) .. .. | 0.53      |
| Magnesia (from MgO lining)   | 0.4       |
| Carbon .. .. .               | 0.88      |
| Chlorine .. .. .             | 0.07      |
|                              | 99.98     |

#### Purification of Metallic Cerium.

The chief impurities of cerium (amounting in the aggregate to about 2 per cent) obtained by the method previously described consisted of iron, cerium oxide, and cerium carbide, of which over 1 per cent was iron.

Owing to the fact that metallic cerium is but slowly attacked by concentrated sulphuric acid, filings of the metal were boiled with this acid. All of the iron was not dissolved, and the method is worthless for purification purposes.

The magnesium alloys of cerium, containing from 50 to 85 per cent cerium, are brittle and may easily be pulverised to a fine powder. When digested with strong sulphuric acid for a few hours, the residue contains cerium, magnesium, and iron. This method is also worthless.

The best method of purification consists in preparing the cerium amalgams. The amalgams are prepared by boiling mercury with cerium in a long iron pipe arranged with a condensing tube at the top. Solid amalgams are easily obtained by this method. The iron and impurities float to the top and may be skimmed off. The amalgams carefully prepared give only a very slight test for iron. The cerium and mercury may be separated by distilling the latter, but this must be done in a high vacuum to prevent oxidation of the cerium. A high temperature is required to drive off all the mercury. The amalgam should be placed in a magnesia vessel, and this in turn heated in an evacuated quartz vessel. The high temperature required would cause the collapse of an evacuated glass vessel.

(To be continued)

**Determination of Sulphur in Insoluble Sulphides.**—Theodor St. Warunis.—To determine the sulphur in an insoluble sulphide 0.5 gm. of the very finely powdered sulphide is mixed with 4 parts of soda and 3 parts of copper oxide, covered with some of the soda-copper oxide mixture, and heated for two hours in a Bunsen burner flame. The mixture must be well stirred with a platinum wire during the heating. After cooling the contents of the crucible are washed out with water and filtered; the residue is boiled with soda solution and washed till the washings are no longer alkaline. Hydrochloric acid is cautiously added to the filtrate, which is then boiled. The solution is evaporated and filtered if silicic acid is present; if it is absent barium chloride is added directly, without previously evaporating the filtrate. The sulphur is thus weighed as sulphate.—*Berichte*, xlv., No. 6.



PROCEEDINGS OF SOCIETIES.

ROYAL SOCIETY.

Ordinary Meeting, June 6th, 1912.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

THE Croonian Lecture was delivered by Dr. KEITH LUCAS on "*The Process of Excitation in Nerve and Muscle.*"

Summary.

Attention has lately been drawn to the slow progress made by physiologists in understanding the physico-chemical nature of the nervous impulse. In the present lecture an attempt is made to examine one aspect of the experimental knowledge which must precede the formulation of any hypothesis of this nature. The first problem is to analyse by experiment the relation between each of the phenomena observed in an excited nerve or muscle and that central disturbance which constitutes the nervous impulse.

This analysis determines what phenomena must be taken into account in any hypothesis of the nervous impulse. It reveals the fact that work on the propagation of the disturbance in nerve and muscle has been hampered by the want of a method by which a quantitative measure of the disturbance might be obtained. It shows also that there can be distinguished from the propagated disturbance a preliminary local excitatory change, which is produced by an exciting agent at the seat of stimulation, and constitutes the necessary condition for starting the propagated disturbance.

By the recognition of the local excitatory process there is opened a fresh possible line of advance in the direction of determining what the nature of the propagated disturbance may be. The former constitutes the condition which initiates the latter, and a knowledge of the physico-chemical nature of the local change may therefore form an important step towards formulating an hypothesis of the nature of the disturbance which is the basis of propagation.

The hypothesis of Nernst, that the local excitatory process is a concentration of ions at a membrane impermeable to those ions, is examined critically. Some objections already brought against it prove unfounded. The genuine difficulties of the hypothesis are in themselves of service in suggesting experimental work which is needed for the complete verification of any such hypothesis. Until such work shall have been done it would be useless to accept or to reject the hypothesis, which remains for the present a valuable means of attack and a guide to future work.

The following papers were read :—

"*Antelope as a Reservoir for Trypanosoma gambiense.*" By Dr. H. L. DUKE.

"*Observations on Fowls and Ducks in Uganda with Relation to T. gallinarum and T. gambiense.*" By Dr. H. L. DUKE.

"*Morphology of the Trypanosome causing Disease in Man in Nyasaland.*" By Sir D. BRUCE, F.R.S., Major D. HARVEY, Major A. E. HAMERTON, Dr. J. B. DAVEY, and LADY BRUCE.

"*Theory of the Algebraic Functions.*" By Prof. J. C. FIELDS, Ph.D.

SOCIETY OF PUBLIC ANALYSTS AND OTHER ANALYTICAL CHEMISTS.

Ordinary Meeting, June 5th, 1912.

Mr. LEONARD ARCHBUTT, President, in the Chair.

MESSRS. Harold Thomas Cranfield, Ernest Gabriel Jones, and William Henry Roberts were elected Members of the Society.

Certificates were read for the second time in favour of Messrs. Stanley Winter Collins and Charles Blüthner Lessner.

The following papers were read and discussed :—

"*Composition of Milk.*" By H. DROOP RICHMOND.

The average composition of milk during 1911 was :—

| Specific gravity. | Total solids. | Fat. | Solids not fat. |
|-------------------|---------------|------|-----------------|
| 1·0317            | 12·51         | 3·71 | 8·80            |

The prolonged drought during the summer affected the quality of the milk, the solids not fat being below the average from July to September, and the deficiency was shown to be due to a deficiency in proteins.

"*Application of Adsorption to the Detection and Separation of certain Dyes.*" By A. CHASTON CHAPMAN and ALFRED SIEBOLD.

The authors point out that the well-known adsorbent properties of kaolin may be usefully applied to the detection and separation of certain artificial dyes, some such as Congo red, Bismarck brown, methylene blue, &c., being removed by shaking up their aqueous solutions with kaolin, whilst others, such as acid magenta, fluorescein, and eosin, are not affected. In cases where two adsorbable dyes are removed by the kaolin, their separation can in some cases be effected by treating the coloured kaolin with alcohol.

In this way good separations of three artificial dye-stuffs have been made in several cases. The stained kaolin can, of course, be submitted to the action of various reagents for the identification of the adsorbed dye.

"*Estimation of Dirt in Milk.*" By W. F. LOWE.

The sediment was first estimated by weight, but it was found to be more accurate to estimate it by volume; control experiments with recent cowdung showed that only one-eighth part by weight could be recovered. The sediment is first examined with the microscope and afterwards tested for bile.

Prosecutions are usually instituted when the sediment amounts to 3 to 4 parts per 100,000 of milk.

"*New Method for the Detection and Estimation of small Quantities of Nitrous Acid.*" By E. HOLL MILLER.

The author shows that when a solution of dimethylaniline hydrochloride is added to an acidulated solution containing nitrous acid, a yellow coloration is developed, due to the formation of paranitrosodimethylaniline. The reaction is a very sensitive one, and can be employed for the colorimetric estimation of small quantities of nitrous acid.

"*Use of Methylene Blue as an Indicator in Iodometric Titrations.*" By FRANK STURDY SINNATT.

A solution of methylene blue may be used as the indicator in iodometric titrations in the presence of ethyl alcohol. Starch indicator is known not to be delicate in alcoholic solutions, and it is suggested that methylene blue may find some special applications for the estimation of iodine in solutions containing alcohol.

"*Determination of Nitric and Nitrous Acids in Acetic Acid Solution. The Stability of Nitric Acid in Acetic Acid Solution.*" By KENNEDY J. P. ORTON and WILLIAM HERBERT GRAY.

The determination of nitric and nitrous acids in acetic acid solution is described. The estimation of the nitric acid depends on the fact that on evaporating the acetic acid solution with a quantity of potassium carbonate slightly in excess of the nitric acid, the whole of the nitric acid remains as potassium nitrate, whilst the nitrite is destroyed. The nitrous acid can be determined directly in the acetic acid solution by Raschig's permanganate method.

It is shown that in acetic acid solution, nitric acid at concentrations of 1—7 per cent is quite stable; the nitrous acid gradually disappears, being partly oxidised to nitric acid. Even when exposed to light the same behaviour is observed; the nitric acid is not reduced.

## CHEMICAL SOCIETY.

Ordinary Meeting, June 6th, 1912.

Prof. PERCY F. FRANKLAND, LL.D., F.R.S., President,  
in the Chair.

THE PRESIDENT referred to the loss sustained by the Society in the death of M. Lecoq de Boisbaudran (elected an Honorary and Foreign Member in 1888) on May 28th.

Messrs. G. F. Wesley Martin, R. Robinson, and C. R. Wilkins were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. James Harry Dyson, North Lea, St. Ives Road, Skircoat Green, Halifax; Sydney Charles Gadd, 31, St. David's Hill, Exeter; Shigeru Komatsu College of Science and Engineering, Kyoto Imperial University, Kyoto, Japan; Ramni Paniker, M.A., M.Sc., care of Messrs. Röhm and Haas, 4, Quai St. Clair, Lyons, France; Hui Chün Tsao, B.Sc., I-Hing, Kiang-Su, China.

Of the following papers, those marked \* were read:—

\*136. "The Vapour Density of Ammonium Nitrite." By PRAFULLA CHANDRA RAY, NILRATAN DHAR, and TINCOWRY DE.

The vapour density of ammonium nitrite as determined by Hofmann's method at a temperature of 66° to 78° conforms to the normal value.

\*137. "Pyrogenic Decompositions. Part I. Benzene." By CLARENCE SMITH and WILLIAM LEWCOCK.

References to the literature show that a substance, produced by the pyrogenic decomposition of an organic compound, is obtained usually in very poor yield; for example, the best yield of diphenyl obtained by the pyrogenic decomposition of benzene is 30 per cent, recorded by Schultz (*Annalen*, 1874, clxiv., 201). In the course of some experiments by one of the authors on the formation of isoprene by the pyrogenic decomposition of American turpentine, the prime importance of temperature and of duration of heating on the course of the decomposition has been made very manifest.

The experience thus gained has been applied in the pyrogenic decomposition of benzene, with the result that a continuously-working apparatus has been constructed, whereby benzene is converted into diphenyl to the extent of 70 per cent of the theoretical yield; solid by-products are formed only in traces.

\*138. "The Absorption Spectra of certain Aromatic Nitroamines and Nitroamides." By GILBERT T. MORGAN, EDGAR JOBLING, and RAYMOND T. F. BARNETT.

The authors have continued the spectroscopic examination of certain of the polynitrated aromatic amines (compare *Trans.*, 1911, xcix., 1945), and particularly of the dinitro-derivatives of this series.

The absorption curve of 2:6-dinitro-*p*-toluidine was found to be quite comparable with that of the tertiary amine, 2:6-dinitro-dimethyl-*p*-toluidine, both bases showing very considerable suppression of the absorption band.

On comparing the absorption spectra of 3:5-dinitro-*p*-toluidine, 3:5-dinitromethyl-*p*-toluidine, and 3:5-dinitro-dimethyl-*p*-toluidine, it was found that only the tertiary amine showed this suppression, both the primary and secondary bases exhibiting a well-marked absorption band, that of the former base being the more persistent.

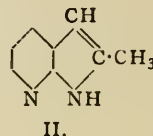
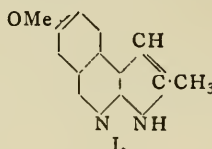
5:6-Dinitro-3-amino-*o*-xylene and 3:5-dinitro-6-amino-*o*-xylene also show this suppression of the band characteristic of the majority of aromatic nitroamines, whereas 3:5-dinitro-4-amino-*o*-xylene, 3:4-dinitro-5-amino-*o*-xylene, and 4:5-dinitro-3-amino-*o*-xylene exhibit selective absorption of the normal type.

Picramide shows two well-defined absorption bands. Toluene-*p*-sulphonyl-1-nitro- $\beta$ -naphthylamine (yellow) and its N-methyl derivative (colourless), and toluene-*p*-sulphonyl-1:6-dinitro- $\beta$ -naphthylamine (colourless) do not exhibit absorption bands, either in the visible or ultra-violet regions of the spectrum.

The aromatic nitroamides exhibit absorption spectra of the same general type without absorption bands, whether the acyl groups are inorganic (NO, NO<sub>2</sub>) or organic (CH<sub>3</sub>·CO, SO<sub>2</sub>·C<sub>7</sub>H<sub>7</sub>, &c.).

\*139. "The Constitution of Harmine." (Preliminary Note). By WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

The authors have commenced a series of experiments on the alkaloids of *Peganum harmala*, and are now in a position to suggest an expression (I.) which readily affords an explanation of the reactions of harmine, and cannot be very far from the true representation of the constitution of this substance:—



The complete argument on which this formula is based cannot be given here, but, in addition to the facts which have already been observed by other workers, among whom O. Fischer is the most prominent, the following new observations have greatly contributed to the solution of the problem. Harmine contains an NH-group and a methyl group, which has the power of condensing with aldehydes, &c., characteristic of the methyl group in quinaldine.

*Benzylideneharmine*, C<sub>12</sub>H<sub>9</sub>ON<sub>2</sub>:CH:CHPh, is obtained by boiling harmine with excess of benzaldehyde, and is purified by conversion into the sparingly soluble bright yellow crystalline hydrochloride.

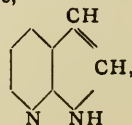
The base separates from ethyl alcohol in pale yellow prisms melting at 191–192°, and its solutions have a most intense violet fluorescence. *p*-Nitrobenzylideneharmine, C<sub>12</sub>H<sub>9</sub>ON<sub>2</sub>:CH:CH·C<sub>6</sub>H<sub>4</sub>·NO<sub>2</sub>, prepared by heating together harmine and *p*-nitrobenzaldehyde, separates from alcohol in red needles, and melts at 266°.

*C-Benzylharmine*, C<sub>12</sub>H<sub>9</sub>ON<sub>2</sub>:CH<sub>2</sub>:CH<sub>2</sub>Ph, obtained by the reduction of benzylideneharmine with zinc dust and acetic acid, crystallises from methyl alcohol in rectangular prisms melting at 138°.

The sparingly soluble hydrochloride separates from water in colourless needles which, in dilute solution, exhibit a blue fluorescence.

*Nor-harminecarboxylic acid*, C<sub>12</sub>H<sub>9</sub>ON<sub>2</sub>:CO<sub>2</sub>H, obtained by the oxidation of benzylideneharmine with potassium permanganate in acid solution, crystallises from acetic acid in the form of the acetate in yellow prisms. This substance loses acetic acid on heating at 100°, or better by treatment with hot water, and furnishes the free acid as a pale yellow crystalline powder, which is almost insoluble, and could not be re-crystallised. Its salts, both with acids and alkalis, are crystalline and sparingly soluble in water. With ferrous sulphate it develops a brownish red coloration, which again clearly indicates that the methyl group in harmine is in the  $\alpha$ -position with respect to one of the nitrogen atoms.

The formula of *apoharmine* (II.) deduced from that suggested for harmine (I.) is that of 2-methylindole, in which one of the methine groups of the benzene ring is displaced by a nitrogen atom. Such substances have not yet been prepared (see, however, the following note), and the properties of such a fused pyridine-pyrrole nucleus are unknown. There can, however, be little doubt that the pyridine ring would greatly modify that of the pyrrole ring, and the structure,—





The distribution of iodine between the solution and the amorphous compounds is in all cases given by an exponential formula, which in the case of saponarin and of cholalic acid only applies over a comparatively short range of concentrations. The blue hydrosol of saponarin

becomes colourless more or less abruptly at a dilution of 1:7000, corresponding with the true solubility, when the whole of the substance becomes molecular-disperse.

#### DISCUSSION.

Prof. MORGAN referred to the interesting point mentioned by the authors that salts of the more electro-positive metals favoured the production of adsorption iodine complexes, and suggested a comparison of the behaviour of caesium with that of barium and lanthanum, since these three elements are the most electro-positive members of their respective families.

142. "The Absorption Spectra of Various Derivatives of Naphthalene in Solution and as Vapours." By JOHN EDWARD PURVIS.

The absorption spectra of various  $\alpha$ - and  $\beta$ -derivatives of naphthalene show that (1) the nature and type of the solution bands is controlled by the nature and type of the substituting atom or group of atoms, and (2) the vapours of these substances exhibit bands which are comparable with the solution bands. These results were discussed with regard to the intrinsic vibratory energy of the molecules and their valencies.

143. "The Velocity of the Hydrogen Ion and a General Dissociation Formula for Acids." By JAMES KENDALL.

The following modification of the conductivity method has been used to determine the velocity of the hydrogen ion. The dissociation constants for weak acids at high dilutions are found to be more or less satisfactory, according to the value employed for the velocity of the hydrogen ion. With acids of a certain limited range of strength (100k between 0.1 and 1.0), one particular value alone will give a satisfactory constant. Experiments have been carried out with several acids and with different samples of water, and the value finally deduced is 347.2 at 25°, with a maximum divergence of  $\pm 0.4$ .

In more concentrated solutions the above acids diverge considerably from the simple dilution law. Their dissociation, however, can be exactly expressed by the formula  $m^2/(1-m)v = k + c(1-m)/m$ .

This formula is intermediate between those of Ostwald and van't Hoff, and has been extended to all types of acids. In all cases the agreement between the calculated and observed values is within the limits of experimental error. The above formula is therefore found to be universally applicable for acids.

144. "N-Chloro-derivatives of Benzylidene-diamides." By FREDERICK DANIEL CHATTAWAY and ALAN EDULF SWINTON.

The benzylidene-diamides which are produced when benzaldehyde is heated with amides, although very easily hydrolysed, yield N-chloro-derivatives with hypochlorous acid.

From benzylidenediacetamide the dichloro-compound has been prepared, but from benzylidenedibenzamide only the monochloro-derivative has been obtained, this, on account of its sparing solubility, being easily isolated. These compounds show the usual general characteristics of chloroamino-derivatives. They are easily hydrolysed, even on long exposure at the ordinary temperature to moist air, benzaldehyde and chloro-acetamide or benzamide being formed.

They react vigorously with warm concentrated potassium hydroxide solution, benzaldehyde, potassium carbonate, and a primary amine being produced. Probably hydrolysis first takes place, the chloro-amide subsequently undergoing the Hofmann transformation under the influence of the alkali hydroxide.

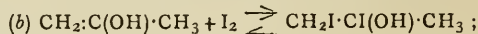
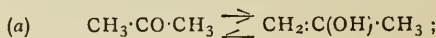
145. "The Refractivity of Sulphur in Various Aliphatic Compounds." By THOMAS SLATER PRICE and DOUGLAS FRANK TWISS.

The densities and refractive indices at 16° and 25° of the various dithio-esters previously prepared by the authors (*Trans.*, 1908, xciii., 1645; 1909, xcv., 1050) have been determined, and the corresponding molecular refractivities

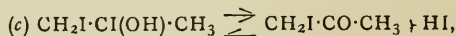
calculated. From the results, the atomic refractivity of sulphur has been deduced, and the values so obtained have been compared with those deduced from sulphur compounds prepared by other investigators, especial reference being made to the optical effect of auxiliary valencies (compare Eisenlohr, *Ber.*, 1911, xlv., 3188).

146. "The Conditions of Isodynamic Change in the Aliphatic Ketones. Part I. The Autocatalytic Reaction between Acetone and Iodine." By HARRY MEDFORTH DAWSON and FRANK POWIS.

If a small quantity of iodine is added to a neutral aqueous solution of acetone, the velocity with which the iodine disappears increases rapidly as the reaction proceeds, in consequence of the catalysing effect of the hydriodic acid which is formed as one of the products of the interaction. The change takes place in three stages:—



and—

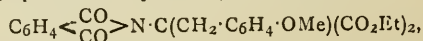


and the halogen acid which is set free in the third stage accelerates the primary isodynamic change in proportion to the quantity present. The observed progress of the change is in agreement with the assumption that the second and third stages in the reaction are of relatively high speed.

The initial velocity of the reaction in "neutral" solution appears to be much greater than can be accounted for on the basis of the original acidity, and experiments, in which small quantities of halogen acid, alkali, and sodium acetate were added to the solution at the start, seem to show that the isodynamic change is accelerated by other than acid catalysts. Although bases probably accelerate the reaction, the observed facts cannot be interpreted on the assumption that the change is conditioned by the presence of acids or bases, and it is suggested that water, independently of its ionising properties, plays the part of an accelerator.

147. "Tyrosine and its Derivatives containing Substituents in the Benzene Ring." (Preliminary Note). By HENRY STEPHEN and CHARLES WEIZMANN.

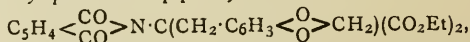
Ethyl phthaliminop-*p*-methoxybenzylmalonate,—



was prepared by heating molecular quantities of *p*-methoxybenzyl bromide, and the potassium compound of ethyl phthaliminomaltonate with xylene in an oil-bath at 145° for six hours. When purified by crystallisation from ethyl alcohol it melts at 83°.

Tyrosine was obtained by hydrolysis of the above compound (a) with concentrated aqueous sodium hydroxide, and subsequent decomposition with concentrated hydrochloric acid according to Sørensen and Andersen's method (*Zeit. Phys. Chem.*, 1908, lvi., 266); (b) with concentrated hydrochloric acid in a sealed tube at 175° for two hours.

Ethyl phthaliminopiperonylmalonate,—



was obtained similarly by condensing piperonyl bromide and ethyl phthaliminomaltonate. After re-crystallisation from methyl alcohol it melts at 89°.

148. "Configuration of the Stereoisomeric Dibromosuccinic Acids." By ALEX. MCKENZIE.

A detailed account of work of which a preliminary note has already been published (*Proc.*, 1911, xxvii., 150).

*l*-Dibromosuccinic acid melts at 157–158°, and has  $[\alpha]_D^{25} -13$ –148° in ethyl acetate solution.

The action of water on the *l*-acid and its barium and silver salts was examined.

(To be continued).



## NOTICES OF BOOKS.

*Methods of Air Analysis.* By J. S. HALDANE, M.D., LL.D., F.R.S. London: Charles Griffin and Co., Ltd. 1912.

THIS book contains a description of apparatus and methods which will be found rapid and convenient for the analysis of air and fairly simple mixtures of gases. A detailed account of the apparatus which the author has devised for the purpose is given, including both the larger form and the smaller and more portable modification of it, and the directions for using both are quite full enough to enable anyone who has had some experience of ordinary gas analysis to carry out the determinations. Methods of calculating results are explained, and some typical results are tabulated. The processes for the determination of small quantities of carbon monoxide and dioxide are described, and also methods of estimating the amount of dust in the air. Most of the methods have previously been described in periodical literature, but physiologists, mine officials, &c., will be glad to have them put together in book form, and will find any alterations which have been made in the directions all tend to make them more explicit.

*Testing, Fault Localisation, and General Hints for Wiremen.* By J. WRIGHT. London: Constable and Co., Ltd. 1912.

SUCH electrical testing as can readily be performed by an average wireman equipped with comparatively simple and inexpensive apparatus is clearly described in this little book. It contains thoroughly practical hints on the localisation of defects, and by means of suitable examples explains to the wireman how to set about his work of testing, making the utmost use of his powers of observation and inference, and not relying simply on rule-of-thumb methods. The directions are given in very simple language. Some general hints are added, and simple repairs, such as the replacement of broken filaments in lamps of the older patterns, are described.

*Smoke. A Study of Town Air.* By JULIUS B. COHEN, Ph.D., B.Sc., F.R.S., and ARTHUR G. RUSTON, B.A., B.Sc. London: Edward Arnold. 1912.

THIS book contains a really remarkable amount of information on the composition of town air. The authors have performed many series of experiments, extending over a great number of years, on the nature of soot and the quantity emitted from domestic and factory chimneys. Their observations relate more particularly to the city of Leeds and the neighbourhood, and they have studied the variations in the amount of soot suspended in the air and the quantities temporarily and permanently deposited, and have brought together many data as to its effects on vegetation and on health. Gaseous impurities are also considered, and the corrosion of masonry, metal work, &c., by sulphuric acid is discussed. Although the authors have not entered into the question of the remedies for the evil of smoke they have done a valuable piece of work in collecting facts as to the incomplete combustion of carbon and the formation of fog.

*Laboratory Experiments in General Chemistry.* By HERMAN SCHLUNDT. Second Edition. Columbia, Missouri: E. W. Stephens Publishing Co. 1912.

THE course of practical chemistry outlined in this book is described as being suitable for first-year college students to whom the subject is new. It is intended to be used both as an introduction to more advanced works and by the student who will take up elementary chemistry only

in the early years of his college work. These two aims can be reconciled only with difficulty, and it is easy to find instances of the subordination of the interests of one class of students to those of the other. But on the whole the good use of the book should tend to make the student think. He is repeatedly asked to find replies to questions by exercising his powers of observation and reasoning, and, on the other hand, when he cannot be expected to arrive at the correct answers unaided he is told where to find the necessary information by reference to Kahlenberg's "Outlines of Chemistry," or to Alexander Smith's "General Chemistry for Colleges." Some of the exercises suggested are of a rather unusual type, such as making an estimate of the comparative cost of a product prepared in the laboratory, and a few seem out of place in an elementary course, as, for example, the preparation of sulphuryl chloride.

## CHEMICAL NOTICES FROM FOREIGN SOURCES.

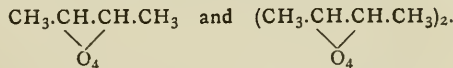
NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

*Berichte der Deutschen Chemischen Gesellschaft,*  
Vol. xlv., No. 6, 1912.

**Silver Spiral for Organic Analysis.**—A. H. Fiske.—In order to prepare a silver spiral for use in organic elementary analysis the author immerses a piece of ordinary copper wire gauze in silver nitrate solution until it is coated with silver. It is then heated in the blowpipe flame until the superficial layer begins to melt. By immersing only half the spiral in the silver nitrate, and then proceeding as before, a combined silver and copper spiral can be obtained.

**Constituent of Ozone.**—C. Harries.—The author has previously suggested that ozone is a mixture and contains a constituent oxozone  $O_4$ , which is decomposed when ozone is washed with caustic soda and sulphuric acid. He now finds that symmetrical butylene yields two kinds of ozonides. With ozone which has been washed with caustic soda and sulphuric acid it gives the normal monomeric ozonide  $CH_3.CH-CH.CH_3$  and the dimeric

product, while with ozone which has not been washed it gives the monomeric and dimeric oxozonides—



The normal monomeric ozonide is unchanged when treated with strong ozone (containing  $O_4$ ). Thus the monomeric  $O_4$  ozonide must be produced by a constituent of ordinary strong ozone, which is decomposed by caustic soda and sulphuric acid. Ordinary 11–14 per cent ozone appears to contain about one-third of oxozone. The study of the action of ozone on other derivatives, e.g., pinene, caoutchouc, &c., seems to confirm these conclusions.

**Double Salts of Chlorides of Rubidium and Cæsium with Ferrous Chloride.**—Ernst Wilke-Dörfurt and Gerhard Heyne.—When a mixture of a solution of iron wire in concentrated hydrochloric acid and a solution of rubidium chloride is allowed to crystallise over sulphuric acid, crystals of di-rubidium chloride, ferrous chloride-dihydrate,  $2RbCl.FeCl_2.2H_2O$ , or of the corresponding monorubidium chloride  $RbCl.FeCl_2.2H_2O$  separate out, according to the proportions of the constituents employed. The cæsium chlorides, which have the same formulæ, can be prepared similarly.

*Bulletin de la Société Chimique de France.*  
Vol. xi.—xii., No. 7, 1912.

**Isomorphism in the Organo-metallic Series.**—Paul Pascal.—The organo-metallic derivatives of silicon, tin, and lead have the same constitution and very similar crystalline forms. They mix in all proportions to give mixed crystals. Hence in the strict sense of the word they must be regarded as isomorphous, which confirms the view that lead is allied to the tetravalent metalloids and metals.

**Determination of Formic Acid by means of Potassium Permanganate in Alkaline Solution.**—A. Fouchet.—Formic acid, either alone or in presence of its homologues, can be determined by the following method:—0.05 gm. of the substance to be analysed dissolved in a little water is added to 40 cc. of a solution of sodium carbonate (50 grms. of crystals per litre) and 50 cc. of a solution of potassium permanganate (5 grms. per litre). The same quantities of permanganate and carbonate are placed in another flask without the formate. The two flasks are then placed for three minutes in a water-bath of boiling water. Twenty cc. of 50 per cent dilute sulphuric acid and 50 cc. of a solution of ferrous sulphate (20 grms.  $\text{FeSO}_4$  and 30 grms.  $\text{H}_2\text{SO}_4$  made up to 1 litre) are added, and the excess of the ferrous sulphate is titrated in each flask with permanganate. The difference of the two volumes of permanganate required to produce a pink coloration represents the quantity of oxygen required by the formic acid— $3(\text{HCOOH}) + 3\text{O} = 3\text{CO}_2 + 3\text{H}_2\text{O}$ .

**Halogen Derivatives of Oxide of Phenyl.**—A. Mailhe and M. Murat.—When chlorine acts on a solution of oxide of phenyl in carbon tetrachloride in presence of a little iodine a liquid is obtained, and may be separated into three fractions by fractional distillation. The first fraction consists chiefly of unchanged oxide of phenyl; the second, distilling at  $270-300^\circ$ , contains the monochlor-derivative; and the third, distilling above  $300^\circ$ , the dichlor-derivative. The bromine compounds can be obtained similarly. These halogen derivatives are relatively stable, and the monoderivatives react with magnesium in ethereal solution.

**Action of Chlorine and Bromine on Dehydrodicarvacrol.**—H. Cousin.—The direct action of bromine on a suspension of dehydrodicarvacrol in chloroform yields the dibrominated derivative  $\text{C}_{20}\text{H}_{22}\text{Br}_2\text{O}_2$ . This is isomeric with dibrominated dithymol. The action of chlorine on dehydrodicarvacrol gives two different substances, according as one molecule of phenol is treated with 4 atoms of chlorine or with excess of the latter. In the first case a dichlor derivative is obtained, and in the second an addition product of the chlorinated quinone. The formula of the first is  $\text{C}_{20}\text{H}_{22}\text{Cl}_2\text{O}_2$ , and of the second  $\text{C}_{20}\text{H}_{22}\text{Cl}_2\text{O}_2 + 4\text{Cl}$ .

**Action of Anisic and Piperonylic Aldehydes on the Monosodium Derivative of Benzyl Cyanide.**—F. Bodroux.—Anisic aldehyde reacts with the sodium derivative of benzyl cyanide to give anisic acid and  $\alpha$ -phenyl-paramethoxycinnamic nitrile. The products in the case of piperonylic aldehyde are piperonylic acid and  $\alpha$ -phenyl-methylene-3,4-dioxycinnamic nitrile.

**Symmetry of Spartein.**—Charles Moureu and Amand Valeur.—The action of methyl iodide on the iodohydrates of spartein and of isopartein gives absolutely analogous results. One of the bases is necessarily asymmetric, but this test gives no clue as to which is the symmetric base. The stereoisomerism of the two iodomethylates of spartein can be established directly, but neither the symmetry nor the asymmetry of spartein has yet been proved.

**Tanning by means of Halogens.**—L. Meunier and A. Seyewetz.—Gelatin can be rendered insoluble by adding to every 10 grms. of gelatin 500 cc. of a saturated solution of chlorine water containing 50 grms. of sodium chloride, and cooling the mixture to  $0^\circ$ . Solutions of hypochlorites act even more readily than chlorine, and with bromine and hypobromites the tanning phenomena are more marked. With skins the actions are analogous, and probably chloramine  $\text{R-NHCl}$  and bromamine  $\text{R-NHBr}$  groups are formed in the albumenoid molecules.

*Atti della Reale Accademia dei Lincei.*  
Vol. xxi., No. 6, 1912.

**Oxysulphides of Antimony.**—E. Quercigh.—The trioxide and trisulphide of antimony are miscible in all proportions in the fused state. A compound is formed corresponding to the formula  $\text{Sb}_4\text{OS}_5$  (i.e.,  $5\text{Sb}_2\text{S}_3 \cdot \text{Sb}_2\text{O}_3$ ); this is decomposed at  $522^\circ$  into crystals of  $\text{Sb}_2\text{S}_3$  and a liquid phase, according to the reversible equation  $\text{Sb}_4\text{OS}_5 \text{ cryst.} \rightleftharpoons \text{Sb}_2\text{S}_3 \text{ cryst.} + \text{liq.}$  Mixed crystals of  $\text{Sb}_2\text{O}_3$  and  $\text{Sb}_4\text{OS}_5$  exist for concentrations between 0 and 18 per cent  $\text{Sb}_2\text{S}_3$ , 16.66 and 23 per cent  $\text{Sb}_2\text{O}_3$ .

## MISCELLANEOUS.

**Chemical Society.**—An Extra Meeting of the Chemical Society will be held at Burlington House, W., on Wednesday, June 26th, at 8.30 p.m., when Sir William Tilden, F.R.S., will deliver the Cannizzaro Memorial Lecture.

**The Royal Photographic Society of Great Britain.**—A House Exhibition of photographs by the late F. P. Cembrano, F.R.P.S., will be held as above, and will be open to the public from Tuesday, June 18th, till Saturday, July 20th, daily (Sundays excepted) from 11 a.m. till 10 p.m. The artistic side of photography has suffered a severe loss by the death of Mr. F. P. Cembrano, F.R.P.S., who for many years delighted the world with his dainty productions. Delicate health, followed by a long and serious illness, withdrew him from his work for a number of years, with the result that to younger workers his pictures are comparatively little known, but photographers whose memories carry them back to the exhibitions of ten years ago will remember how eagerly they looked forward to seeing the latest thing by him. Mr. Cembrano's tastes and sympathies were wide enough to include all sections of the art, and English landscapes had a strong attraction for him; it was, however, by his charming studies of Spanish scenery, and above all of views in the Alhambra, that he was popularly known. A collection of some fifty of his photographs are now on view at the House of the Royal Photographic Society, at 35, Russell Square, and will remain open, free, to the public daily from 11 a.m. till 10 p.m. until Saturday, July 20th. The collection comprises fifteen views in the Alhambra and the South of Spain, and thirty-seven of English landscapes, chiefly of river scenery. Admirers of Mr. Cembrano's work should make a point of seeing these pictures before they are dispersed.

## MEETINGS FOR THE WEEK.

**THURSDAY, 27th.**—Royal Society. "Electrical Vibrations on a Thin Anchor Ring," by Lord Rayleigh. "Molecular Statistics of some Chemical Actions," by Hon. R. J. Strutt. "Morphological Studies of Benzene Derivatives—III., Paradibromobenzene-sulphonates (Isomorphous) of the 'Rare Earth' Elements—a means of Determining the Directions of Valency in Tervalent Elements," by H. E. Armstrong and E. H. Rodd. "Optical Rotatory Dispersion—Part I., The Natural and Magnetic Rotatory Dispersion in Quartz of Light in the Visible Region of the Spectrum," by T. M. Lowry. "Apparent Change in Mass during Chemical Reaction," by J. J. Manley. "Diurnal Variations of the Electric Waves occurring in Nature, and on the Propagation of Electric Waves round the Bend of the Earth," by W. H. Eccles. "Report on the Total Solar Eclipse of 1911, April 28," by Rev. A. L. Cortie.

**FRIDAY, 28th.**—Physical. "Hysteresis Loss as affected by Previous Magnetic History," by E. Wilson, B. C. Clayton, and A. E. Power. "Efficiency of Generation of High-frequency Oscillations by means of an Induction Coil and Ordinary Spark Gap," by G. W. O. Howe and J. D. Feattie. "Dielectric Hysteresis at Low Frequencies" by W. M. Thornton. "Resistance to the Flow of Water along a Capillary Soda-glass Tube at Low Rates of Shear," by A. Griffiths and Miss C. H. Knowles. "Self-demagnetisation of Steel," by S. W. J. Smith and J. Guild.



# THE CHEMICAL NEWS.

VOL. CV., No. 2744.

## THE NITROGEN ENRICHMENT OF SOILS.\*

IN a paper recently read before the Royal Society of Canada the authors gave a summarised account of the experiments that had been conducted by the Chemical Division of the Experimental Farms since 1889 in the very important matter of the nitrogen enrichment of soils ("Experimental Work towards the Nitrogen Enrichment of Soils," by Frank T. Shutt, M.A., F.I.C., Dominion Chemist, and A. T. Charron, M.A., May, 1912).

The first fact brought forward was that rich productive soils are characterised by a high nitrogen and humus content. Evidence was adduced to show the correctness of this statement, not only from the examination of cultivated soils of first quality and established high productiveness, but from many analyses of soils of the virgin prairie of the North-Western provinces so widely recognised for their wonderful fertility.

On the other hand, soils naturally poor and those impoverished by irrational farming have been found to be low in nitrogen and humus forming material. The semi-decomposed vegetable matter of the soil is the natural storehouse of its nitrogen, and experimental proof had been obtained that demonstrated beyond question that humus forming material must be constantly added to cultivated soils if their nitrogen content and their productiveness were to be maintained. The grain growing of the West, which implies fallowing and no formation of a sod, was very destructive of humus and nitrogen, and must in time seriously impair the richest soil. The rational and economic upkeep of soil fertility demands the keeping of stock for the production of manure—the most important natural source of humus and nitrogen for farming lands—and a proper rotation of crops; that is, one which will periodically enrich the soil, as by the growth of a legume, in these valuable constituents.

Nitrogen is the dominant element among those furnished by the soil, and its amount and availability in a very large measure determine crop yield. The investigations discussed in this paper were instituted to learn the extent of the depletion of the soil's nitrogen by cropping and cultural operations, how far the legumes (clover, alfalfa, vetch, &c.) could be utilised on the farm for the increase of the soil's nitrogen and the furnishing of humus forming material, and finally to ascertain what the practical value might be of inoculation (a) with "cultures," and (b) with soil from fields bearing a leguminous crop for the encouragement of the growth of these plants.

### Depletion of Soil Nitrogen.

It was found from the examination of a soil which had never received manure and which had been under cultivation for twenty-two years, during which period it had borne six crops of wheat, four of barley, and five of oats, with nine summer fallows (bare) during the latter seventeen seasons, that the loss of nitrogen to a depth of 8 inches amounted to 2206 lbs. per acre. Of this, approximately 700 lbs. had been removed in crops. This means that about 1500 lbs. per acre, or 68 per cent of the total nitrogen lost, had been dissipated during this period through cultural operations, fallowing, &c. The soil experimented with was an exceedingly rich prairie soil in Saskatchewan. Very probably it is a type of soil that would at first lose nitrogen more rapidly than one of a poorer quality, and, further, undoubtedly, fallowing is of all operations the most

wasteful of soil fertility, but the figures are significant in showing there is an inevitable and heavy depletion of the soil's most valuable constituent, consequent upon the necessary tillage of the land. Our soils, then, must be constantly replenished with organic matter if they are to be kept productive and profitable.

### Legumes as Nitrogen Enrichers.

As is well known the legumes are very rich in nitrogen, and as a part of this nitrogen at least is obtained from the atmosphere, they as a class are extremely valuable as manurial agents. The more important leguminous crops, clovers, alfalfa, vetches, peas, beans, &c., were grown and analysed, the weight and nitrogen content of stem, leaves, and roots per acre being determined. The clovers and alfalfa were found to be the most valuable, chiefly by reason of their larger root system, in which might be stored from one-third to one-half the total nitrogen in the crop. By the turning under of a fair growth of one of these crops, from 100 to 150 lbs. of nitrogen may be added to the soil per acre, an amount equivalent to that furnished by an application of 10 tons of ordinary barnyard manure.

The details of an interesting and valuable experiment were given, in which by analysis of the soil "before and after" the amount of nitrogen which had become part and parcel of the soil through the growth of clover was determined. A plot of very light sandy loam was first seeded with clover in 1902. Every second year from that date until the present time the plot had been dug over and re-sown. No manure at any time was used, but phosphoric acid and potash were furnished at the outset by a moderate dressing of superphosphate and muriate of potash. The soil was sampled and analysed six times during the experiment period. The data show that the nitrogen content had practically doubled in the nine years despite the losses from bacterial activity and other causes. The soil to a depth of 4 inches contained at the beginning of the experiment (1902) 533 lbs., and at the close (1911) 1005 lbs. per acre. If it is assumed that the growth of the clover had added annually nitrogen at the rate of 100 lbs. per acre. it will be observed that the loss due to oxidation, &c., during the experiment period almost equalled the gain.

If the clover had been cut and fed, the manurial value of the residues (roots, decayed leaves, &c.) would have been almost one-half that here recorded. These data afford satisfactory evidence as to the value of a leguminous crop in the rotation, if soil fertility is to be economically maintained.

### Inoculation Experiments.

The special value of the legumes as nitrogen enrichers is due to the fact that they are able to draw upon the free nitrogen of the atmosphere for a part of their supply. Thus, instead of impoverishing the soil's store like all other crops, they add to it. The appropriation of free nitrogen does not take place directly, but is accomplished through the agency of certain bacteria present in the soil, and which attach themselves to the roots of the legume, with the result that nodules or tubercles are formed thereon in which they reside. In some way, not as yet clearly understood, nitrogen compounds are formed within these nodules, and enter into the circulation of the host plant, to be built up into its tissues of root, stem, and leaf. It is the nitrogen of the air existing in the interstices of the soil that these special nitrogen-fixing micro-organisms utilise, and this points to the desirability of a well drained, well aerated soil if these bacteria are to perform their beneficial function. Without the aid of these specific bacteria the legumes cannot avail themselves of the free nitrogen of the air, but like other crops draw upon the nitrates of the soil for their nitrogenous food. Legumes, therefore, in the absence of these germs are not nitrogen enrichers of the soil. Are these nitrogen-fixing bacteria universally present in the arable soils of the Dominion? We cannot say that they are, though the examination of the roots of legumes collected in various parts of Canada has shown by the

\* A Contribution from the Chemical Division, Dominion Expt. Farms, Canada.

nodules thereon that these micro-organisms are very widely distributed over the Dominion. Our observations have made very clear that failure to obtain a good catch and growth of clover is not always to be attributed to the absence of the necessary bacteria, but in many instances is due rather to an unfavourable mechanical condition of the soil, inadequate drainage, deficiency of moisture, acidity or sourness of the soil denoting the need of lime, or finally to poor seed.

To furnish the farmers with the means of introducing the nitrogen-fixing bacteria, where their absence is suspected, "cultures" of these bacteria have been prepared and put on the market. Their use is known as inoculation. During the last twenty years a considerable number of these cultures or preparations, from Germany, United States, and home sources, have been tried on the Experimental Farms, and at other points. Specific cultures for clover, alfalfa, peas, beans, &c., have been experimented with. While in many instances they distinctly favoured the growth of the legume, their action on the whole was more or less uncertain. The profitable employment of these preparations seems therefore problematical. All the failures met with were not attributed to lack of vitality in the cultures, but it was evident that their usefulness is much impaired by age, light, and heat, and unless prepared by a reputable firm or institution, and still fresh, satisfactory results can scarcely be looked for.

The employment, as an inoculating material, of the soil from the surface of a field bearing a luxurious crop of the specific legume had given much better results than the use of cultures, and this method, where cost of transportation is not too great, will be found the most reliable for the general farmer. Notable instances of successful inoculation by this method, applying the soil at the rate of 100 to 300 lbs. per acre, were recorded for alfalfa in the North Western provinces. Inoculation, as has been said, is not generally necessary, but where it is considered indispensable by reason of the absence of the nitrogen assimilating bacteria, a supply of this bacteria-laden soil will, it is believed, prove more effective than the use of a culture.

Ottawa May 30, 1912.

## THE PREPARATION AND PROPERTIES OF METALLIC CERIUM.\*

By ALCAN HIRSCH.

(Concluded from p. 294).

### Physical Properties of Metallic Cerium.

IN the determinations of the physical properties, metal of approximately 98 per cent of cerium was used, unless otherwise specified.

1. *Atomic Weight*.—The atomic weight of cerium, determined from pure salts, is 140.25.

2. *Specific Gravity*.—The specific gravity determinations were made in a 50 cc. pycnometer of cylindrical form, with thermometer ground in central neck and with fused-in capillary tube at side. The liquids used were pure benzene and toluene, which have no chemical action on cerium. Several different specimens of metal were used for these determinations. The weight of metal taken varied from 3.4 to 11.2 grms. The average of determinations gave 6.92 at 25° C.

3. *Molecular State of Aggregation*.—No reference was found in the literature as to the crystallographic properties of cerium. Attempts were made by the writer to obtain crystals, but without success. The interior of many ingots of cerium were highly crystalline, especially in the centre of blow-holes. The best condition for crystal growth is

slow cooling from the molten condition. In order to aid the formation of crystals, a small quantity of cerium was melted under lithium chloride. The crucible was kept just hot enough to prevent the lithium chloride from solidifying, and was maintained at this temperature for several hours. The melting-point of lithium chloride (about 550°) is somewhat below the melting-point of cerium, and under these conditions the formation and growth of crystals would be expected. However, no definite crystals of cerium were obtained.

In order to examine the inner structure of cerium, photomicrographs of different specimens were made. The specimens were prepared by dry-polishing, and were etched with alcoholic HCl. An examination of these photomicrographs shows homogeneity of structure.

4. *Hardness*.—For the determination of hardness the scleroscope was used. The hardness of cerium varies, depending upon whether the surface of the metal is rolled, freshly cut, or old. The average value of the hardness for rolled surface was 25.9. The average for freshly cut surface was 9.5. (The reading 100 is the hardness of the standard steel test plate).

5. *Tenacity*.—Cerium is malleable and highly ductile. A strip of cerium was rolled to a thin sheet of a thickness of 0.015 mm. Cerium metal can easily be cut with a knife or scissors, and can be machined fairly well, although there is some tendency for the metal to buckle, as does lead.

6. *Electrical Conductivity*.—In order to make these measurements, a test bar was necessary. A good method of obtaining a known length and cross-section of metal is to take a short piece of capillary tubing, apply suction at one end, insert the other in the molten metal, and so fill the tube. On account of the corrosive action of cerium on glass and silica, it was impossible to use this method.

It was difficult to cast cerium into solid rods, owing to its rapid oxidation in air. The following mould was prepared, which was so designed that molten cerium could quickly be poured into it from the melting crucible and oxidation prevented:—A wrought-iron pipe,  $\frac{1}{2}$  in. (0.65 cm.) inside diameter and about 5 ins. (13 cm.) long, was screwed into the iron base. A piece of cast iron was turned on the lathe to the shape of a small funnel, and was screwed into the wrought-iron pipe. The cerium was melted in a magnesia-lined graphite crucible under a covering of fused salt. The mould was heated to a dull redness, and the entire contents of the crucible poured suddenly into the mould. Very little oxidation or burning of the metal occurred. A rod of cerium 3 ins. (7.5 cm.) long was obtained. This metal contained 93.6 per cent cerium and 4.5 per cent iron. Although the inside of the pipe had been carefully cleaned, it was impossible to prevent contamination of the cast cerium with iron. As it was necessary to pre-heat the mould, a small amount of iron oxide necessarily formed, and, on contact with cerium, was reduced to metal and entered the rod as an impurity. The rod was turned down to size on the grinder.

The electrical conductivity measurements were made by the voltmeter-ammeter method. The potential drop was taken over 1 inch of test bar, and all measurements were made at room temperature. The current was varied from 6 to 18 amperes. The specific resistance of the sample was found to be 71.6 microhms per centimetre cube.

7. *Magnetic Properties*.—Stefan Meyer has measured the magnetic susceptibility of many metals, among them that of cerium (*C. Bl.*, 1899, [2], clxiii., 740). He gives the atomic magnetic susceptibility of cerium ( $K \times 10^{-6}$ ) equal to 34. He does not state the purity of the cerium used. The writer made no attempt to measure the magnetic susceptibility of cerium, but simply to determine if cerium is dia- or para-magnetic.

A small piece of cerium was suspended by a silk thread in a magnetic field of intensity about 5000 lines per cubic centimetre. The metal so tested was paramagnetic, but not strongly so.

Cerium amalgam practically free from iron was sealed

\* A Paper presented at the Twentieth General Meeting of the American Electrochemical Society, Toronto, Canada, September, 1911. From the *Journal of Industrial and Engineering Chemistry*, iii., No. 12.



in a small glass tube and tested in a magnetic field. It was weakly but definitely paramagnetic. From these determinations it was concluded that pure cerium is paramagnetic.

8. *Melting-point.*—It was impossible to use the ordinary thermocouple method to determine the melting-point, as no suitable protecting mantle could be found. Silica and porcelain are both attacked by cerium at its melting-point. Magnesia, which is unattacked, is too porous a material for this purpose.

An attempt was made to obtain a cooling curve of cerium. About 60 grms. of the metal were melted in a magnesia crucible in an electric resistor furnace, and readings were taken with a small copper-constantan couple placed in a porcelain mantle. It was thought that although the porcelain would be attacked somewhat, an approximate value for the melting-point might be obtained. However, the cooling curve showed no constant temperature period, and was worthless.

A small piece of cerium was attached to two long copper wires by means of small copper bolts and nuts, such as are used by watchmakers. Good electrical connection was obtained in this manner. The cerium was placed in a long Jena glass tube, sealed at one end and closed at the other by means of a rubber stopper, and so arranged that the tube could be evacuated. This was then placed in a tube furnace containing a calibrated thermocouple. A small amount of current was passed through the cerium, and when connection was severed an electrical gong sounded. This scheme of obtaining the melting-point did not work, as the rubber stopper connection did not give a perfectly air-tight joint. The small amount of air in the tube combined with the cerium as the temperature increased. This caused a higher vacuum to be produced, with the result that more air entered the tube, and, upon subsequent repetition of this process, all the cerium was oxidised before the melting-point was reached.

The approximate melting-point was determined by heating a small quantity of cerium in a magnesia-lined graphite crucible and reading the temperature at which the metal softened by means of a thermocouple placed just above the metal. This crude method gave the approximate melting-point as about 700°.

The real melting-point of cerium was determined as follows:—A small piece of cerium foil was fastened to two bent platinum wires by means of small copper bolts and nuts, and placed in a small glass bulb and the platinum wires sealed through the glass. The bulb was then evacuated by means of a mercury rotatory pump, and sealed. A small incandescent lamp was connected in series with the cerium, which was heated in an electric muffle furnace. The temperature was read by a calibrated thermocouple. The melting-point of the cerium was very definite, and occurred at a temperature of 635° C. The tube collapsed somewhat, but the method gave satisfactory results.

9. *Ultimate Strength.*—The same test bar was used for these determinations as in the electrical conductivity measurements. The ultimate strength was determined in an Olsen testing machine. The average diameter of the test bars was 0.212 in. (0.55 cm.) There was no elongation with constant load at 350 pounds (159 kg.). The test bar broke with a snap (like cast iron) at 495 pounds (225 kg.). The ultimate strength is equal to 12,900 pounds per square in. (9 kg. per sq. mm.).

10. *Specific Heat.*—The specific heat was determined in a Joly differential steam calorimeter. The principal difficulty encountered was to get a suitable method of protecting the cerium from attack by the steam. The cerium was sealed in a glass tube, but this method was unsatisfactory, owing to the time necessary for exchange of heat due to the small conductivity of the glass. Another method employed for protecting the cerium was to coat it with a mixture of amyl acetate in collodion. However, this coating was attacked by the steam and was liable to

peel. The metal was also placed in a small nickel box, but was attacked by the steam. The best method of protecting cerium, at the same time allowing for rapid heat interchange, was to wrap the cerium tightly in several thicknesses of tinfoil. Blanks were run on copper and tinfoil to check the accuracy of this calorimetric method. The value for the specific heat of copper obtained with this steam calorimeter was equal to 0.0925. The specific heat of cerium (20—100°) was measured and found equal to 0.0524. Mendeléeff gives the specific heat of cerium equal to 0.05 ("Principles of Chemistry," vol. ii., p. 106).

11. *Heat Conductivity.*—No measurements were made on the heat conductivity, and no references were found in the literature relative to this property. The heat conductivity seems to be fairly high, and, if so, cerium is probably one of the exceptional metals which has a low electrical conductivity and high thermal conductivity.

12. *Latent Heat of Fusion.*—From observations on melting cerium, the latent heat of fusion seems to be fairly high. It has not been determined to my knowledge.

13. *Heat of Oxidation.*—The heat of oxidation was determined in a Mahler bomb calorimeter. Cerium must not be burned in contact with platinum, as it will alloy with the latter. The cerium filings were placed in a small magnesia crucible in the calorimeter. From 1 to 2 grms. of cerium filings were used for each determination, under an oxygen pressure of about 14 atmospheres. The average value of the heat of oxidation was 1740 calories per gm., or 60,900 calories per gm. equivalent ( $\text{CeO}_2 = 243.600$ ). These values are probably correct within 4 or 5 per cent. It is difficult to obtain an accurate value for the heat of oxidation where the products of combustion are non-volatile. The determinations in the case of cerium were unusually difficult to make, for the following reasons:—The metal should be in a finely divided form, but preferably in the shape of filings. When cerium is filed, care must be taken to prevent oxidation, owing to the low kindling point. A small amount of oxide forms in any case, and therefore makes the sample of metal taken non-uniform. If the filings are too coarse, oxide will fuse on the surface, and the metal in the interior will be unoxidised. Many of the difficulties encountered in the determination of the heat of oxidation of silicon were met with here (H. N. Potter, *Trans. Am. Electrochem. Soc.*, 1907, xi., 259).

14. *Single Potential.*—Attempts were made to measure the single potential of cerium in the alcoholic solution of cerium chloride. No reliable measurement could be obtained owing to the rapid formation of a film on the polished surface of the metal as soon as current flowed. The potential rapidly decreased as soon as the film appeared, which is almost instantaneous with the passage of current.

Measurements on the decomposition potential of the anhydrous mixed chlorides in absolute alcohol were made, using platinum electrodes. Gas was evolved at an applied electromotive force of 3.5 volts.

As the single potential of cerium could not be measured successfully, its value was calculated from the thermal data taken from Matignon's article on the anhydrous mixed chlorides:—

Heat of formation of  $\text{CeCl}_3$  (per 3Cl) = 270 calories  
Heat of solution of  $\text{CeCl}_3$  .. .. = 33 calories

The calculated decomposition potential of normal cerium chloride in aqueous solution is equal to 4.3 volts. Therefore the single potential of cerium in normal solution of its chloride measured against the normal calomel electrode is equal to -3.16 volts.

15. *Thermo-electromotive Force.*—Two small glass cells, protected by asbestos and fitted with wooden covers, were used. Standard thermometers with small stirrers attached were inserted through the cover. Cottonseed oil was used for the bath, and one of the cells was heated internally by means of several coils of resistance wire. The electromotive force was determined by the potentiometer method

with a special piece of apparatus specially prepared for this kind of work. The thermo-electromotive force of cerium against copper is given in the table below and in the curve shown in Fig. 9. The current flowed at the hot junction from copper to cerium. The measurements are given in the following table:—

| Hot junction.<br>°C. | Cold junction.<br>°C. | Electromotive force.<br>Volts. |
|----------------------|-----------------------|--------------------------------|
| 49.2                 | 29.2                  | 0.000075                       |
| 100.0                | 25.0                  | 0.000770                       |
| 100.0                | Red. to 30.0          | 0.000250                       |
| 151.0                | 26.9                  | 0.000399                       |
| 151.0                | Red. to 30.0          | 0.000387                       |
| 200.5                | 29.7                  | 0.000504                       |
| 200.5                | Red. to 30.0          | 0.000502                       |

16. *Optical Properties.*—Cerium alone could not be used, owing to the fact that a thin film of oxide forms on the polished surface. Different alloys of cerium were tried, and the best ones for this purpose were found to be the magnesium-cerium alloys. The preparation of samples had to be done very carefully, as fine emery and rough entered the soft surface of the cerium. Dry-polishing

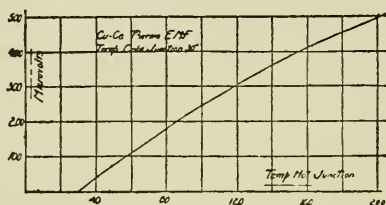


FIG. 9.

with a very fine file (the finest obtainable) was the most satisfactory way of preparing the sample. For the methods of measurement of the optical properties the reader is referred to the article on the subject by Ingersoll and Littleton on "A New Method of Determining the Optical Constants of Metals" (*Phys. Rev.*, xxxi., 489). The constants determined on the magnesium-cerium alloys are given in the table below:—

| Per cent cerium. | n.   | k.   |
|------------------|------|------|
| 83               | 1.60 | 1.74 |
| 61               | 1.43 | 2.30 |
| 26               | 0.73 | 4.79 |
| Pure Mg          | 0.32 | 12.0 |

#### Chemical Properties of Metallic Cerium.

Metal of approximately 98 per cent cerium content was used in these determinations.

Cerium is very slightly attacked by cold water, but in boiling water a slow evolution of hydrogen gas occurs, and the metal is tarnished black. At room temperature the following solvents have no action on cerium: ethyl alcohol, amyl alcohol, chloroform, carbon tetrachloride, concentrated sulphuric acid, concentrated ammonium hydroxide, concentrated sodium hydroxide. Ethyl ether has a very slight action on the metal, as have also 3 per cent and 30 per cent hydrogen peroxide at room temperature. The action of dilute sulphuric acid, concentrated and dilute hydrochloric acid, concentrated and dilute nitric acid, in the cold, is moderately vigorous. Ammonium chloride and potassium chloride, at room temperature, have moderate action on the metal. This may be explained by the fact that in water a small amount of cerium hydroxide forms which is soluble in potassium chloride and ammonium chloride, thus causing fresh surface of the metal to be exposed and resulting in moderate attack of the metal by the solvent. At boiling temperature the following solvents did not attack the metal, chloroform, carbon tetrachloride, concentrated sulphuric acid, concentrated

ammonium hydroxide. The metal was only slightly attacked by the following solvents at boiling temperature: ethyl alcohol, amyl alcohol, ethyl ether, and concentrated sodium hydroxide. Dilute nitric acid, ammonium chloride, potassium chloride, and 3 per cent hydrogen peroxide at boiling temperatures gave moderate action. Dilute sulphuric acid, concentrated and dilute hydrochloric acid, concentrated nitric acid, and 30 per cent hydrogen peroxide gave vigorous evolution of gas at boiling temperature.

The action of various gases on cerium was studied. A small amount of cerium filings was placed in a porcelain boat in a hard glass tube. The air was displaced by the gas under test, and the tube heated gently by means of gas burners. The cerium filings heated in chlorine emitted a very bright light at a temperature of 210° to 215° C. The salt formed was tested and found to be anhydrous cerous chloride.

In bromine, cerium burned at a temperature of 215° to 220° C. with emission of less light than in the case of chlorine. The salt formed in solution in water, and was identified as the bromide.

In iodine vapours no light was emitted, although the tube was heated to a temperature of 300° C. On examination of the contents of the tube it was found that some iodide had formed.

Cerium burned with luminescence when heated in air to a temperature of 160° C. If a lump of cerium is sealed in a glass bottle and kept warm for some time, a black powder is seen to form upon the surface of the cerium, and when the bottle is opened this powder ignites at room temperature. This is probably due to the formation of a highly pyrophoric suboxide of cerium.

When cerium filings are heated to 345° in hydrogen gas, the hydride forms without emission of light. The hydride has been described and studied by Muthmann (*Matignon, Comptes Rendus*, [22], cxxxi., 891; Muthmann and Bauer, *Liebig's Annalen*, ccxxv., 281).

Cerium filings were heated in nitrogen to a temperature of 1000° C. No luminescence was observed, but some nitride was formed. This nitride is a black powder, and has been studied and described by Matignon (*Comptes Rendus*, [21], cxxxi., 837).

When the nitride is heated in potassium hydroxide solution, evolution of ammonia gas occurs. When exposed to air the nitride gradually changes over to a brown oxide.

Cerium filings were heated in the vapours of sulphur. When the black substance which is formed is treated with dilute sulphuric acid, sulphuretted hydrogen is evolved. Cerium sulphide has been studied by various investigators (Didier, *Comptes Rendus*, 1885, c., 1461; Muthmann and Stutzel, *Ber.*, 1889, xxxii., 3413).

Cerium filings were heated to a temperature of 500° C. in an atmosphere of carbon monoxide. There was no visible reaction, but part of the filings appeared oxidised.

#### Alloys.

A number of different alloys of cerium were studied, and are described below. In most cases the alloys were high in cerium, usually containing about 70 per cent cerium. The metals were weighed out in the proper proportions, using from 5 to 10 grms. of cerium. The cerium was first melted in a small porcelain crucible under a layer of sodium chloride, and the other metal added in small pieces. The porcelain crucible was, of course, attacked by the cerium, but it was found that a thin layer of silicide of cerium forms, and this protects the crucible from further attack. The metal can in most cases be removed without breaking the crucible if care is exercised, and therefore one crucible serves for several melts. The silicide does not appear as a contaminant in the alloy. Porcelain crucibles were used except in cases where especially pure metal was desired, when magnesia crucibles were employed.

The work on the alloys of cerium is presented below in an epitomised form. The time at the writer's disposal was such that a complete study of each alloy could not be



made. However, specimens of all the alloys described have been preserved, and will be used for future references.

**Silver.**—Silver alloys with cerium quietly, and the thermal change appears to be small. The alloy has a silvery-white lustre, and is hard and brittle. From all appearances a compound is probably formed between cerium and silver.

**Gold.**—When gold was added to molten cerium there was a slight flash from the crucible, but the reaction was not violent. The alloy was fairly soft, and had a reddish appearance. It disintegrated somewhat on ageing, forming a purplish black powder.

**Platinum.**—The reaction between cerium and platinum appeared to be endothermic. The alloy was fairly hard and was pyrophoric. It disintegrated to a slight extent when aged.

**Copper.**—The cerium-copper alloy was hard and brittle, although the two component metals were soft and malleable. A compound is probably formed. The alloy disintegrated to a powder.

**Tin.**—This alloy was formed with the evolution of much heat. When first made, the alloy was pyrophoric, but on standing for a few months a powder formed, showing that the alloy disintegrated slowly when exposed to the air.

**Antimony.**—There was considerable evolution of heat on the formation of this alloy. The alloy was very soft, and was non-pyrophoric. It did not oxidise nor disintegrate on ageing.

**Arsenic.**—The reaction appeared to be exothermic. The alloy was fairly soft and somewhat pyrophoric. It did not decompose on being kept.

**Carbon.**—Carbon and cerium combine directly when heated together. The carbide has been referred to and described earlier in this article.

**Silicon.**—Cerium and silicon form the silicide  $\text{CeSi}_2$ . This compound may be formed by the reduction of the oxide of cerium. Large amounts of the mixed silicides have been prepared by the writer. The following mixture is recommended for their preparation:—

|                          | Grms. |
|--------------------------|-------|
| $\text{MgO}_5$ .. .. .   | 1000  |
| Powdered graphite .. ..  | 200   |
| Powdered silicon .. .. . | 450   |

The silicide of cerium is somewhat brittle, and may easily be pulverised to a fine powder. It is a splendid reducing agent. When the silicide is added to cerium so that the silicon content is about 15 per cent a good pyrophoric alloy is obtained.

**Sulphur.**—The preparation of the sulphide has been referred to earlier in this article.

**Selenium.**—Some reference is found in the literature to the selenide of cerium. Mosander reduced the selenite in a stream of hydrogen and obtained a brown substance of a disagreeable odour. Moissan has shown that the selenides may be obtained by the action of selenium fumes on cerium carbide.

Selenium was added to molten cerium. The reaction was very vigorous, and was accompanied with the evolution of reddish fumes. The melt consisted of two portions, a powder and a metallic alloy. The powder was impure cerium selenide, and the alloy, which was pyrophoric, apparently consisted of the selenide dissolved in excess cerium.

**Tellurium.**—No reference was found in the literature to the telluride of cerium. Tellurium combined vigorously with molten cerium, giving a brownish pulverulent mass, which was probably the impure telluride. When treated with dilute acids, the well known odour of hydrogen telluride was detected.

**Lead.**—When lead was added to molten cerium, a violet reaction occurred, causing a portion of the contents to be ejected from the crucible. The alloy was very soft, and emitted sparks of a reddish colour when scratched with a file. The alloy disintegrated slightly on ageing.

**Calcium.**—Calcium alloyed with cerium quietly, without evolution of much heat. The alloy was white and was harder than either constituent. When scratched with a file it emitted a cluster of bright sparks. It is stable in air, oxidising very slowly. The alloy did not disintegrate.

**Sodium.**—Sodium alloyed with cerium quietly. The alloy was hard and slightly pyrophoric. It oxidised somewhat when exposed to air.

**Aluminium.**—Aluminium alloyed with cerium fairly quietly. The alloy was very hard and brittle. It disintegrated without oxidation. A compound of aluminium and cerium was probably formed. This alloy was not pyrophoric.

**Zinc.**—The combination of cerium and zinc was accompanied by a vigorous, in fact, almost explosive, reaction. There was a large amount of heat evolved. The alloy was hard, brittle, and pyrophoric, and remained unoxidised when exposed to atmospheric conditions.

**Cadmium.**—Cadmium and cerium combined vigorously with considerable heat evolution. The alloy was hard, brittle, and pyrophoric. On exposure to air a film of oxide formed slowly, but the alloy did not disintegrate.

**Chromium.**—The alloy was white in colour, hard, and brittle. It was somewhat pyrophoric. It remained unchanged in the air.

**Manganese.**—Manganese combined quietly with cerium, forming a fairly hard pyrophoric alloy, stable in air.

**Iron.**—The iron-cerium alloys are very interesting, as they were the first pyrophoric alloys known, and were discovered by Dr. Auer von Welsbach. The alloys of about 70 per cent cerium content are fairly hard and somewhat brittle. It is seen that the structure is heterogeneous, probably consisting in part of a cerium-iron compound. These alloys have been the subject of some discussion in the literature (*Zeit. Electrochem.*, 1908, xiv., 549; Fattinger, *Chem. Ztg.*, 1909, xxxiii., 1113; C. R. Behm, *Ibid.*, 1910, xxxiv., 361, 367), as have the reasons for the pyrophoric properties (Fattinger, *Ibid.*, 1910, xxxiv., 469; Samter, *Ibid.*, 1910, xxxiv., 52). The writer believes that the question of the pyrophority depends upon the following factors; cerium alone is soft and malleable, and when scratched with a file small particles are not broken off. However, when the alloy is hard and brittle, small particles are easily detached from the mass, and the friction is sufficient to raise the temperature of these small particles to the incandescent point of cerium ( $160^\circ$ ). As metallic compounds (such as  $\text{Cu}_3\text{Sn}$ ) are as a rule hard and brittle, the addition of such compounds to cerium usually assures a pyrophoric alloy. The alloy should be high in cerium, so that ignition occurs at a low temperature, and should contain excess of cerium above that required for the formation of a compound (such as  $\text{CeSi}_2$ ) to act as a binder and so prevent the disintegration of the alloy, as in the case of the cerium-aluminium alloy containing about 60 per cent cerium.

**Nickel.**—The nickel-cerium alloys made were similar to the iron alloys, but were somewhat softer. The ones high in cerium were very pyrophoric.

**Tungsten.**—Powdered tungsten equivalent in weight to 15 per cent was added to molten cerium. The tungsten dissolved fairly quickly, and the reaction was quiet. The alloy was hard, brittle, and pyrophoric.

**Mercury.**—Cerium forms amalgams fairly easily. Their preparation has already been described under the methods of purification. The amalgams containing only 1 or 2 per cent of cerium are liquid, but the ones of higher percentage are solid. These amalgams oxidise easily in the air, and those containing 8 or 10 per cent cerium take fire in the air.

**Magnesium.**—The whole series of these alloys were prepared, and have been discussed under optical properties. The alloy containing about 83 per cent cerium is highly pyrophoric. Most of these alloys are brittle, and can be easily pulverised. Excellent flashlight powders can be prepared from the ones of higher cerium content. These alloys also form splendid reducing agents, as the combination of cerium and magnesium is an endothermic reaction,

and when the alloy is oxidised, more heat is emitted than from an equivalent mechanical mixture of the two constituents. The fact that the alloys of from 60 to 75 per cent cerium content may be easily pulverised in a mortar to a fineness of 200 mesh should render these alloys valuable for thermal reductions. A small amount of metallic vanadium was prepared by reducing  $V_2O_5$  by this method. The alloys of from 75 to 85 per cent cerium content can be pulverised, but they are so highly pyrophoric that it is difficult to prevent igniting them.

## NOTES ON A NEW FORM OF EXTRACTION THIMBLE.\*

By P. A. BOECK.

THE following notes have been collected from the experiences of a number of different investigators using the new type of inorganic extraction thimbles known as "Alundum."

A few words as to the nature of these thimbles may be of interest:—Alundum, the material from which these articles are made, is the product of the fusion of the mineral bauxite (a natural hydrate of aluminium carrying small percentages of iron oxide, silica, and titanium oxide) in the electric furnace, in which process partial purification takes place so that the resulting product is essentially pure fused alumina. This material has been used quite extensively for abrasive purposes, replacing emery and corundum, over which it has the advantage of being absolutely uniform and of easily controlled composition. It can be made to yield an abrasive higher in crystalline alumina and consequently of higher abrasive efficiency than any other form of commercial natural aluminous abrasive.

In the manufacture of laboratory articles of this material, the fused alumina is crushed, graded to uniform mesh, mixed with a small amount of a suitable ceramic bonding material, and burned at a high temperature in an ordinary porcelain kiln, where the bond is caused to vitrify or mature, giving it the strength of an ordinary porcelain body, and at the same time retaining its porous nature, which allows the penetration and filtration of liquids and gases.

The porosity of the bodies can be controlled in several ways, which depend, to a certain extent, on the other physical properties, such as strength, thermal conductivity, texture, melting-point, expansion due to temperature changes, shrinkage, &c., which are desired. The three methods most generally used in obtaining bodies of different porosities are:—(1) By varying the size of the grain or particles of the alundum, thereby changing the size of the voids; (2) by changing the kind; and (3) the amount of bonding materials used. By combining these factors, suitable bodies may be obtained having any texture or porosity for the penetration of liquids of any density. The state of subdivision of the residue which is to be separated from the liquid or gas is of course the final criterion of the permissible size of the voids. In organic extraction work it is particularly desirable to have a porous medium which gives the most rapid filtration possible with the complete retention of the residue.

Another feature of these thimbles is the fact that no blank extractions have to be made to be sure that the materials are fat-free, as in the case of paper or other organic materials, as, being of a refractory nature, they can be readily cleaned by being ignited at a temperature high enough to dispel any organic material. This also allows of their repeated and indefinite use, so long as no easily fusible inorganic material is ignited in them.

Messrs. Ross and Benner, in their work at the Agricultural Experiment Station at the University of Arizona,

\* Presented at forty-fifth meeting of the American Chemical Society, at Washington, December, 1911. From the *Journal of Industrial and Engineering Chemistry*, iv., No. 4.

on the filtration of soil solutions and the separation of "black alkali" in certain characteristic western soils, showed that filters of this material not only filtered more rapidly without changing the concentration of the solution and absorbed less than any other type of filter on the market, but required less washing, were very much more durable, and could be cleaned and sterilised by igniting at the proper temperature.

For the extraction and filtration of tanning materials, Mr. R. C. Oberfell describes in the *Journal of the American Leather Chemists' Association* for November, 1911, an ingenious device in which a porous Alundum dish substitutes the asbestos mat, or the mixtures of asbestos and kaolin, for removing the insoluble material in tanning materials. Absolutely clear filtrates were obtained in from a half to two minutes without the use of any asbestos or kaolin mixtures in these dishes as against from eighty-two to a hundred and thirty minutes using the official method of filtration with the mat, at a consequent saving of about 98 per cent of the time of filtration, the results of the analyses in each case checking within the allowable error. Where the dish alone was used, no previous saturation or preparation of the filtering medium was necessary, as is the case in the official method.

For organic extraction work on rubber, vulcanised products, fats, waxes, soaps, bitumens, cereals, &c., the proper filtering body for any solvent can be easily made, and is apparently limited only by the texture, which must be fine enough to retain the residue and prevent it from penetrating the pores of the thimble. Rapidity of flow and extraction can in this way be increased many times over that obtained with the ordinary extraction thimble.

The chemist of a large rubber reclaiming plant in the west has recently had made an ingenious type of thimble, consisting of two thimbles semi-circular in cross-section, so made that when fitted together side by side they occupy no more room than a single thimble, allowing two samples to be extracted at the same time in the same solvent. This method would apply, of course, only in cases where the residues only were desired, the filtrates from the two samples being mixed. The scheme worked out very well at a great saving of time and solvent, and there is no reason why this idea could not be followed out further, and any number of sectional extraction thimbles made to fit one extraction tube.

The application of this type of inorganic extraction thimble has not been limited to liquids, as recent tests indicate that it can be used successfully for the filtration of gases and the separation of dust and fume from air, smoke, producer gas, &c., quantitatively.

## PROCEEDINGS OF SOCIETIES.

### ROYAL SOCIETY.

Ordinary Meeting, June 13th, 1912.

Sir ARCHIBALD GEIKIE, K.C.B., President, in the Chair.

PAPERS were read as follows:—

"Expansion Apparatus for making Visible the Tracks of Ionising Particles in Gases, and some Results obtained by its Use." By C. T. R. WILSON, M.A., F.R.S.

The method of making visible and photographing the tracks is essentially that described in a previous communication. Water is made to condense on the ions while still in the positions which they occupy immediately after their liberation by the ionising agent. The apparatus has been enlarged and otherwise improved, and the photographs are now free from the distortion which was a serious defect in those of the earlier paper.

The paths of  $\alpha$ -particles are generally straight or nearly so until within about a mm. of the end (in air at atmo-



spheric pressure) where they become bent. A few, however, show absolutely sudden deviations through considerable angles much earlier in their course. Photographs of complete  $\alpha$ -ray tracks, starting from atoms of radium emanation within the cloud chamber, have been obtained, and show a characteristic head of intense ionisation at the origin.

Portions of the tracks of  $\beta$ -particles from radium have been photographed, the individual ions set free being made visible by the cloud particles condensed upon them, so that they may readily be counted.

The photographs of the clouds formed when a narrow beam of X-rays is sent through the cloud chamber show the tracks of cathode or  $\beta$ -particles starting within the primary beam and extending for some distance beyond it.

There is no indication of any action of the X-rays other than the production of the corpuscular rays.

The corpuscular rays appear to start in all directions, showing no preference for that of the primary beam.

Such photographs show at once the number of cathode rays produced in a gas by a beam of X-rays, as well as the character and length of their paths.

The cloud trails left by many of the corpuscles are resolvable into their component drops so that the ions may be counted.

When the X-rays are allowed to traverse the gas before its expansion, it is possible to separate the positive and negative ions by an electric field before the formation of the clouds, so that the cathode ray tracks appear double in the photographs.

"A Chemically Active Modification of Nitrogen, produced by the Electric Discharge." IV. By Hon. R. J. STRUTT, F.R.S.

1. Active nitrogen is a highly endothermic body, but its energy is of the same order of magnitude as that of other chemical substances.

2. In the reversion of active to ordinary nitrogen, the number of atoms ionised is a very small fraction of the whole number concerned in the change. The ionisation is a subordinate effect, and may be due to light of very short wave-length emitted in the reaction.

3. Additional experiments are described to prove that the change of active nitrogen is more rapid at low temperatures. This is thought to be connected with the monatomic character of the molecule, and to throw light on the connection between temperature and velocity of reaction in other cases.

"Series Lines in the Arc Spectrum of Mercury." By Prof. J. C. McLENNAN.

"Constitution of the Mercury Green Line  $\lambda = 5461$  A.U., and on the Magnetic Resolution of its Satellites by an Echelon Grating." By Prof. J. C. McLENNAN.

"Convergence of Certain Series Involving the Fourier Constants of a Function." By Prof. W. H. YOUNG, Sc.D., F.R.S.

"Classes of Summable Functions and their Fourier Series." By Prof. W. H. YOUNG, Sc.D., F.R.S.

"Number of  $\beta$ -Particles emitted in the Transformation of Radium." By H. G. MOSELEY.

The number of  $\beta$ -particles emitted at the disintegration of each atom has been determined by measuring the current carried *in vacuo* by the radiation from a known quantity of active material. It is found that one atom of radium B and an atom of radium C together emit 2.20  $\beta$ -particles on an average; that an atom of radium B emits the same number of particles as an atom of radium C, and that an atom of radium E appears to emit less than one  $\beta$ -particle. From measurements of the ionisation produced by active deposit of radium emitting a measured number of  $\beta$ -particles, the number of ions produced by a  $\beta$ -particle per cm. of path in air has been calculated. This number varies approximately as  $\lambda^3$ , where  $\lambda$  is the absorption coefficient

of the radiation for aluminium. Hence, using the data of Geiger and Kovarik for the ionising power of the  $\beta$ -radiation from a radio-active atom, the number of  $\beta$ -particles emitted by an atom of uranium X, actinium D, and thorium D has been calculated. From measurements of the number of secondary  $\beta$ -particles produced by the  $\gamma$ -rays, it has been deduced on certain assumptions that an atom of radium C emits two  $\gamma$ -rays. A secondary radiation is set free in surfaces traversed by  $\beta$ -rays. This radiation closely resembles the  $\delta$ -rays, but does not leave the surface unless assisted by an electric field.

"Portland Experiments on the Flow of Oil." By S. D. CAROTHERS.

"Form of the Solution of Laplace's Equation Suitable for Problems Relating to Two Spheres." By G. B. JEFFERY.

"Emission Velocities of Photo-electrons." A. LL. HUGHES, M.Sc., B.A.

This investigation was undertaken to determine the relations between the maximum velocity with which electrons are emitted from metallic surfaces illuminated by ultra-violet light and (a) the wave-length of the light and (b) the nature of the metal. The form which this relation takes is given, more or less definitely, by different theories of the photo-electric effect; and therefore criteria between different theories would be given by accurate experimental evidence on these two relations. Two laws connecting the maximum emission velocity and the wave-length have been suggested. The first, due to Ladenburg, is that the maximum velocity is proportional to the frequency. The second, based originally on the quantum theory, is that the energy of the fastest electrons is proportional to the frequency.

The experimental evidence, at present available, is inadequate to discriminate between the two theories. From the experiments which have been published on the velocities of photo-electrons, it is clear that the velocities vary enormously with the state of the surface. The effect is due to the presence of a variable gaseous film on the surface which reduces both the velocity and the number of the electrons passing through. In this research, metallic surfaces were prepared in such a way that it is extremely unlikely that any surface film could be formed. The maximum velocities of the photo-electrons from a continuously forming surface of mercury was measured. Surfaces of Ca, Mg, Cd, Zn, Pb, Bi, Sb, As, Se, and ZnCl<sub>2</sub> were prepared by distillation in a liquid-air vacuum and were exposed to the light without having been in contact with air or any other gas. From experiments on these surfaces of distilled metals, it was concluded that the maximum energy, and not the maximum velocity, of the photo-electrons was proportional to the frequency. The range over which this is established is from  $\lambda$  1849 to about  $\lambda$  3000. The results can be expressed in the form  $V = kn - V_0$  where  $V$  is the velocity of the photo-electrons measured in volts,  $n$  is the frequency, and  $k$  and  $V_0$  are constants. For cadmium, which may be taken as typical, the values of  $k$  and  $V_0$  are  $3.66 \times 10^{-15}$  and 3.49 volts respectively. The maximum velocity of photo-electrons produced by  $\lambda$  1849 is therefore 2.44 volts. It was found that the values of  $k$  and  $V_0$  changed from one metal to another. The variations of  $k$ , which were only a little larger than the possible errors of experiment, followed the variations in  $V_0$ . For elements of the same valency (given by the number of the group in which they are placed in the Periodic Table)  $k$  and  $V_0$  increase as the atomic volume decreases.

The product of  $V_0$  and  $e$ , the charge on the electron, is interpreted as the work required to separate an electron from a molecule. It is greatest for the electro-negative elements. Knowing the longest wave-length capable of producing appreciable ionisation in air, and assuming a mean value for  $k$ , the work required to ionise a molecule of air was calculated. This agrees well with Demmer's value of the energy required to ionise a molecule of air.

## CHEMICAL SOCIETY.

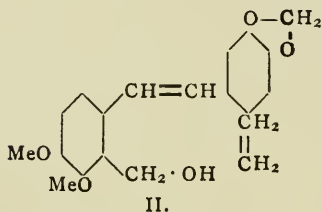
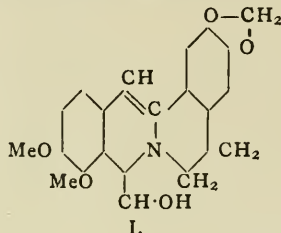
Ordinary Meeting, June 6th, 1912.

Prof. PERCY F. FRANKLAND, LL.D., F.R.S., President,  
in the Chair.

(Concluded from p. 298).

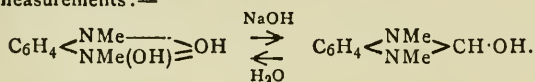
149. "The Exhaustive Alkylation of Tetrahydroberberine." By JAMES WALLACE McDAVID, WILLIAM HENRY PERKIN, jun., and ROBERT ROBINSON.

The authors have combined tetrahydroberberine (I.) successively with benzyl chloride and with methyl iodide, and, by decomposing the final product with alcoholic potassium hydroxide, have obtained a substance (II.) free from nitrogen, which they propose to name *berberilene* :—

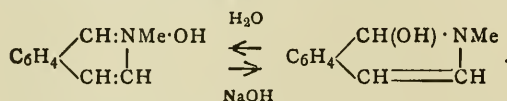


150. "The Spectroscopic Investigation of the Carbinol-ammonium Base Isomerism. Benziminazole and isoquinoline Derivatives." By CHARLES KENNETH TINKLER.

The transformation of dimethylbenziminazolium hydroxide into the corresponding carbinol, dimethylbenziminazolol, and the reverse change of carbinol into ammonium base, has been followed by ultra-violet absorption spectra measurements :—



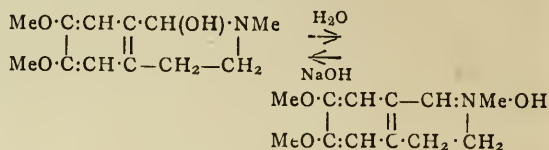
In the case of the *isoquinoline* derivatives, evidence was obtained of the conversion of 2-methyl*isoquinolinium* hydroxide into 1-hydroxy-2-methyl-1 : 2-dihydro*isoquinoline* by the action of sodium hydroxide and of the re-conversion of the carbinol into the ammonium base by the action of water, as recently suggested by Decker (*Journ. Prakt. Chem.*, 1911, [2], lxxxiv., 425) :—



By this method of investigation it appears also that the substituted *isoquinoline*, tarconine methiodide, yields a  $\psi$ -base.

The *isoquinoline* base obtained by Pyman by the oxidation of laudanose (*Trans.*, 1909, xcv., 1266) gives spectra in ethereal, chloroform, and sodium hydroxide solution, which are almost identical with those of the hydro-derivative and  $\psi$ -cyanide of the base, whereas in aqueous solution the spectra of the base are in very close agreement with those of the quaternary salts of the base. From the spectroscopic results obtained with this substance it would appear that the base is more correctly represented as the

closed chain carbinol 1-hydroxy-6 : 7-dimethoxy-2-methyl-tetrahydro*isoquinoline* than as the open-chain aldehyde 4 : 5-dimethoxy-28-methylaminoethylbenzaldehyde, as suggested by Pyman. The base resembles in all respects cotarnine and hydrastinine, which have previously been investigated by this method (Dobbie, Lauder, and Tinkler, *Trans.*, 1903, lxxxiii., 598; 1904, lxxxv., 1005). As in these cases it appears that by the action of the water the true ammonium base is produced :—



151. "Some Derivatives of Oxazole." By JOSEPH LISTER and ROBERT ROBINSON.

A number of aryl-oxazoles have been prepared by the dehydration of acylated amino-ketones in order that their fluorescence and ultra-violet absorption spectra might be investigated.

152. "Electrolytic Reduction. Part VII. The Catalytic Action of Copper." By HERBERT DRAKE LAW.

It has been discovered that finely divided copper exerts a powerful catalytic action on the course of reduction of the  $\alpha\beta$ -unsaturated ketones and aldehydes of the aliphatic and alicyclic series. These compounds are reduced more rapidly on copper than lead, but at the same time the latter metal combines with the partly reduced product. Copper, on the other hand, remains unattacked. The nature of the reduction reaction varies with different compounds. The attack may take place either at the carbonyl group or the unsaturated linking, or at both simultaneously. Hydrocarbons, saturated and unsaturated alcohols, saturated carbonyl compounds, and complex double molecules are formed either singly or in mixture.

153. "The Two Sulphides of  $\beta$ -Naphthol." By CECIL REGINALD CRYMBLE, KENNETH ROSS, and SAMUEL SMILES.

Henriques (*Ber.*, 1894, xxvii., 2999) has shown that  $\beta$ -naphthol sulphide (m. p. 211°) may be converted into another sulphide of lower melting-point (153°) by oxidation and subsequent reduction of the product; it has also been claimed that these sulphides are stereoisomeric. The authors have compared some reactions of these compounds, and the evidence bearing on the relationship between them was considered. The conclusion was drawn that the hypothesis of stereoisomerism is insufficient, and that the two sulphides differ in their atomic structure.

154. " $\alpha$ -Hydroxyhippuric Acid and a New Test for Hippuric Acid." By PAUL HAAS.

$\alpha$ -Hydroxyhippuric acid is prepared by adding bromine to a gently warmed mixture of hippuric acid and red phosphorus suspended in carbon tetrachloride, and pouring the resulting mixture into water.

The test for hippuric acid depends on its conversion into  $\alpha$ -hydroxyhippuric acid, and the subsequent hydrolysis of this substance to benzamide and glyoxylic acid, the latter being detected by the addition of a protein solution and concentrated sulphuric acid.

155. "The Constitution of the Aldol Bases." By MURIEL GWENDOLEN EDWARDS, RALPH EDDOWES GARROD, and HUMPHREY OWEN JONES.

The two "aldol bases,"  $\text{C}_{12}\text{H}_{17}\text{ON}$ , prepared from *m*-4-xyldine and acetaldehyde, were studied by Jones and White (*Trans.*, 1910, xcvi., 633), and it was found that they were interconvertible by the action of acids, but not by the action of heat; both gave the same benzoyl compound, the same oxime, and the same condensation product with *m*-4-xyldine, but they gave different nitroso-derivatives.

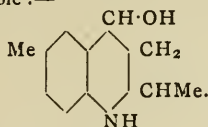
In order to arrive at a definite conclusion as to the cause of this interesting case of isomerism, the study of these



compounds has been extended, and the corresponding bases obtained from *p*-toluidine,  $\psi$ -cumidine, and 3-bromo-*p*-toluidine have been examined. The clue to the solution of the problem was found when it was established that the isomeric aldol bases from *p*-toluidine gave two different monobenzoyl compounds, and that the nitroso-derivatives of these bases could be benzoylated.

It was then found that by treatment with acetyl chloride in pyridine solution diacetyl derivatives could be prepared, and in a similar way two isomeric dibenzoyl derivatives were obtained from the xylidine aldol bases.

These observations can only be accounted for on the assumption that the isomeric aldol bases are the *cis*- and *trans*-stereoisomerides of hydroxytetrahydroquinoline derivatives, for example:—



in the case of the *p*-toluidine compounds.

This view explains all the known facts, and also accounts for the non-formation of similar compounds from mesidine and 5-bromo-*m*-4-xylidine.

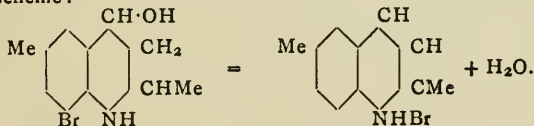
The hydroxytetrahydroquinoline ring must be capable of fission very easily on account of the formation of the oxime, the interconversion of the isomerides by acids, and the formation of the same condensation product with xylidine in the case of the aldol bases derived from xylidine.

These condensation products, the double Schiff's bases, appear to precede the aldol bases in the interaction of acetaldehyde and amines, and as they give monobenzoyl and mononitroso-derivatives their structure is best represented as  $C_6H_4Me \cdot NH \cdot CHMe \cdot CH_2 \cdot CH \cdot N \cdot C_6H_4Me$ .

156. "Some Quinoline and Tetrahydroquinoline Derivatives obtained from Aldol Bases." By RALPH EDDOWS GARROD, HUMPHREY OWEN JONES, and PERCY EDWIN EVANS.

During the study of the constitution and properties of the "aldol bases" and their conversion under the influence of heat, or of acids into quinoline and tetrahydroquinoline derivatives, the behaviour of the aldol bases derived from  $\psi$ -cumidine and 3-bromo-*p*-toluidine has been studied. The former are converted either by heat or by acids into a mixture of 2:5:6:8-tetramethylquinoline (m. p. 27—28°) and 2:5:6:8-tetramethyltetrahydroquinoline in equimolecular proportions.

When the aldol base of 3-bromo-*p*-toluidine is heated to 180—200° it changes quantitatively into the hydrobromide of 2:6-dimethylquinoline, according to the following scheme:—



On boiling with acids, however, 8-bromo-2:6-dimethylquinoline (m. p. 96—97°) and 8-bromo-2:6-dimethyltetrahydroquinoline are produced, together with a small quantity of 2:6-dimethylquinoline and hydrogen bromide.

157. "The Viscosity of Ether-alcohol Mixtures." By FRANK BAKER.

The viscosities of mixtures in different proportions of the following ethers and alcohols have been observed:—Methyl, ethyl, and propyl alcohols; ethyl ether, anisole, and phenetole.

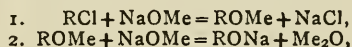
From the results obtained, it was concluded that dissociation of the alcohol and association to an ether-alcohol complex took place in these mixtures. The bearing of these results on the viscosity of mixtures in general was discussed, and the relation  $\gamma^n = a\gamma_1^n + (1-a)\gamma_2^n$  shown to be empirical.

158. "Morphotropic Relationships between Racemic Compounds and their Optically Active Components." By GEORGE JERUSALEM.

The author has examined crystallographically a number of optically active and racemic compounds, and studied the relationship observable between the crystalline structure of racemic compounds and their optically active components in these and many other cases. In all the instances examined it is found that a close morphotropic relationship exists between these substances, and that the relationship is precisely of the kind foretold by the theory of Barlow and Pope concerning the connection of crystalline form with chemical composition and constitution.

159. "The Action of Sodium Methoxide on 2:3:4:5-Tetrachloropyridine." (Part I.). By WILLIAM JAMES SELL.

As is well known, halogen derivatives of pyridine, when heated with sodium methoxide, frequently give rise to hydroxy- instead of methoxy-compounds, but no satisfactory explanation of this reaction has hitherto been offered. The author finds that when 2:3:4:5-tetrachloropyridine is heated to 205° with sodium methoxide in a sealed tube, a mixture of gaseous products is produced, mainly composed of methyl ether and hydrogen. It is suggested that the methoxy-derivative of pyridine first formed reacts with the excess of sodium methoxide to produce methyl ether, thus:—



and that the hydrogen is produced by the action of sodium hydroxide on the methyl alcohol present with production of sodium formate and hydrogen.

## PHYSICAL SOCIETY.

Ordinary Meeting, June 14th, 1912.

Prof. A. SCHUSTER, F.R.S., President, in the Chair.

A Demonstration of the Use of Specific Gravity Balls for Determining very Small Differences of Density was given by Mr. T. H. BLAKESLEY.

The present communication was made for the purpose of pointing out that the sensibility of specific gravity balls was, as a matter of fact, vastly underrated by scientific men, and the author quoted passages from Prof. Balfour Stewart and Mr. Fownes which would tend to produce the belief that beyond the third decimal place specific gravity balls are not trustworthy. A variety of experiments was quoted which would indicate a sensibility a hundred times as great as this, and indeed that the error which might be expected in a properly conducted experiment would be of the order 5 in the sixth decimal place. The author has been in the habit for the last quarter of a century of employing specific gravity balls for the purpose of discriminating between the qualities of potable waters in respect of density and, therefore, of hardness, of testing the efficacy of softening processes, &c., for all of which the specific gravity ball is admirably suited. His process of observation differs from the ordinary rough-and-ready use in the fact that a thermometer of fairly open scale is employed to give the temperature at which a specific gravity ball is in equilibrium with a liquid which is being slowly warmed or cooled through that point of temperature. The error in such a temperature observation should not amount to more than three or four hundredths of 1° C.

If such a determination is made in distilled water at ordinary atmospheric temperatures it fixes the specific gravity of the ball at the temperature of equilibrium within four or five units in the sixth place of decimals. If a second observation with the same ball is made in a slightly heavier liquid, say, common tap-water, the temperature of equilibrium will be considerably higher, perhaps 2 deg. or more, than in distilled water. By applying the coefficient

of cubical expansion the density of the ball at the higher temperature can be obtained, and this is the density of the second specimen of water at the second temperature. Reference to a table of densities of distilled water will furnish its density at the higher temperature, and the difference between the two numbers will give what the author calls the density excess of the second liquid over distilled water at the higher of the two temperatures. This density excess is best quoted in parts in one million. For example, the density excess for a specimen of London water was found to be 290 at  $17^{\circ}\text{C}$ .

For a few degrees on either side of this value this number is sensibly constant, a fact of some value, as it enables one to employ four or five balls at the same time in one experiment.

One noteworthy result of experiments made through a long course of years is that simple glass balls tend to expand, especially in the years immediately succeeding their manufacture. The rise of the zero point of thermometers has led to the belief that glass contracts with age.

Mr. Blakesley then proceeded to explain the sort of apparatus which he thought might make the extreme sensibility of the specific gravity ball available for quickly detecting the infusion of fresh water in the ocean due to the presence of icebergs in the neighbourhood. This problem is one which cannot be decided without definite experiments made upon water specimens taken from the sea at various noted distances from icebergs, observing direction of wind and current at the times of taking the specimens. These could be quietly submitted to examination, and the results would be of the first importance in settling some of the details of the apparatus for quick practical determination of fresh water infusion.

#### DISCUSSION.

Dr. CHREE remarked that there was also a similar gradual change in the density of hydrometers with time. He questioned whether the density of sea-water was uniform enough, especially near land, in order to apply Mr. Blakesley's test for icebergs.

Mr. A. CAMPBELL asked how far dissolved gases affected the density of water. He asked whether the secular change in the balls might not be due to a change of weight on wearing.

Prof. C. H. LEES inquired whether the degree of accuracy obtained was greater than Dr. Warrington obtained with the same method seven or eight years ago.

Mr. F. E. SMITH pointed out that the secular change in the balls might be due to the solubility of glass. If the balls were made of soft soda glass and the water were alkaline such a loss of weight could be seen in ten minutes.

The PRESIDENT pointed out that the secular change in these bulbs was quite a different phenomenon from the secular change in thermometers. With respect to the application of the method to the detection of icebergs he did not think it would be much help. What was wanted was not to detect the presence of a field of ice which was generally known, but some particular iceberg that was dangerously near.

The AUTHOR, in reply, remarked that a couple of balls which had iron wire inside them did not show the secular change of density. He had not tested the balls for loss of weight. A slight solubility of the glass was not detrimental, since the balls could be standardised in distilled water as often as desired. Unlike hydrometers the balls eliminated all surface action.

A paper on the "Maximum Sensibility of a Duddell Vibration Galvanometer" was read by Dr. H. F. HAWORTH.

The maximum sensibility of a moving coil vibration galvanometer as a voltage detector is obtained when the flux through it is so adjusted that the back E.M.F. of the coil is equal to its CR drop; then the back E.M.F. is equal to half the applied voltage, and the current is equal to  $V/2R$  and is in phase with the applied voltage.

Increases of current sensibility of about 30 per cent at 200 vibrations and 40 per cent at 1000 vibrations were obtained on running the instrument in a vacuum, thus showing that a large part of the mechanical work produced was used in overcoming the molecular friction of the system. Tables and curves are given showing the variations of voltage and current sensibility with alteration of flux, &c.

#### DISCUSSION.

Mr. A. CAMPBELL remarked that he had convinced himself that the chief energy loss in his vibration galvanometer was in the elastic hysteresis of the wires. In Duddell's galvanometer the moving wires are so light that he thought it might be otherwise, but Dr. Haworth's paper showed that the damping was still chiefly due to the same cause.

A paper on "An Accurate Examination of the Steinmetz Index for Transformer Iron, Stalloy, and Cast-Iron" was read by Mr. F. STROUDE.

These experiments were undertaken to provide a sound experimental basis, suitable for mathematical analysis, with a view to discovering, if possible, some relation connecting hysteresis loss and flux density which will accord with results obtained practically to a greater extent than the empirical law due to Steinmetz.

The method of uniformly varying flux was used for the determinations. The magnetic treatment given to the specimen by this method approximates to that received by iron employed in alternating-current work, whilst the method admits of a very high degree of accuracy.

Experiments were made with transformer iron stalloy (3 per cent silicon iron) and cast-iron, two rings of each material being tested.

The rings were carefully demagnetised before testing, and even reduced to a cyclical state for each current value before making observations.

A set of comparative tests on one of the transformer iron rings was made by the ballistic method, and these tests show that, in general, for a given value of B the hysteresis loss, and the value of H for the ballistic tests are higher than the corresponding values for the slow cyclic tests.

The results were expressed in the form of the Steinmetz equation  $w_h = \eta B^2$ .

For transformer iron  $\epsilon$  has the value 1.7 between the limits  $B = 1000$  and  $B = 17,000$ . Stalloy gives a value of  $\epsilon = 1.66$  between  $B = 4000$  and  $B = 12,000$ , having somewhat higher values for lower values of B. In the case of cast-iron  $\epsilon$  is equal to 1.82 between the limits  $B = 2000$  and  $B = 6000$ , rising for lower flux densities. It will be seen that the material with the highest maximum permeability has the lowest constant "index" and *vice versa*.

The work of previous experimenters has been consulted, and values of " $\epsilon$ " at different flux densities deduced from their experimental results.

It is hoped before long to publish results obtained at the lower and upper extremes of magnetisation.

#### DISCUSSION.

Dr. RUSSELL thought the results in this paper would be most useful.

Mr. A. CAMPBELL suggested that the author should try the effect of annealing the transformer iron, which will then sometimes give an index of nearly 2. The losses at low values of B were very important, and the results so far were very discordant. It is of importance to know the energy loss in telephone cables that are loaded by winding iron strip round them. Here the value of B would be very small, probably 50 or 100.

Prof. C. H. LEES remarked that there were interesting scientific problems raised by the constancy of the index over so wide a range.

Prof. G. W. O. HOWE remarked that the index seemed to go off to infinity for very low values of B, indicating that the hysteresis fell very rapidly.

Prof. J. T. MORRIS drew attention to the accuracy of the present work. He pointed out that in order to find explanations for the losses experiments should be made at high



temperatures, above  $700^{\circ}\text{C.}$ , or as where the B and H curves are of simple character. The hysteresis loss is then zero for values of B less than a certain amount, and constant for all values greater than another fixed value, and a linear function of B between these two ranges.

## NOTICES OF BOOKS.

*Qualitative Organic Analysis.* By F. B. THOLE, B.Sc. (Lond.), F.C.S. London: Methuen and Co., Ltd. 1912.

ALTHOUGH qualitative organic analysis has hitherto been a much-neglected subject there are indications that it is now beginning to occupy its rightful place as a very valuable factor in the training of the chemist, and there is much need for good and reasonably-priced books on the subject. Such a one will be found in this work, which is partly reprinted from Dunstan and Thole's "Text-book of Practical Chemistry." The author develops his subject in the most logical fashion, doing his utmost to discourage any haphazard work, and the student who follows his directions will get a good practical knowledge of methods of carrying out various operations, such as fractional distillations and crystallisations, which will be most useful to him in his later work, and, moreover, he will be handling and learning the appearance and properties of a large number of important substances. The method of analysis recommended for an unknown organic substance involves three stages:—Firstly, the elementary analysis of it; secondly, the determination of its chemical family; and, finally, the identification of individual members of the family by special reactions or by the preparation of derivatives. Melting- and boiling-point determinations (the results of which are fully tabulated) are performed only for confirmation.

*An Introduction to Quantitative Analysis.* By S. J. M. AULD, D.Sc. (Lond.), Ph.D., F.I.C., F.C.S. London: Methuen and Co., Ltd. 1912.

THERE are many features in this book which will recommend it for use as a preliminary text-book of quantitative analysis, more particularly for the student who has access to the larger treatises on the subject, but who requires a moderate-sized laboratory guide of his own. It gives clear working directions for a fairly extended but not intensive course of quantitative work. Very little space is given to the discussion of the theoretical side of quantitative analysis, though the theory of indicators is treated perhaps rather more fully than is usual in a book of the size. Volumetric work is first described, and all the usual estimations are included, the only one of practical importance which is omitted being that of phosphates by means of uranium solution. A short course of gasometric work follows, in which the use of the simplest kinds of apparatus, e.g., Lunge's nitrometer and Hempel's gas burette, is shortly described. Electrolytic work is also treated in a very short section which would probably have to be very extensively supplemented by the demonstrator in the laboratory or by reference to other books. In Part IV. a few special separations and some technical analyses are described; these include the analysis of water, alloys, and minerals. The last section of the book is devoted to determinations of vapour density, and of a few combining weights which can be found accurately by the elementary student, using only simple apparatus.

*Die Fabrikationen von Bittersalz und Chlormagnesium.* ("The Manufacture of Epsom Salts and of Magnesium Chloride"). By Chemiker Dr. Phil. AUGUST BERGE. Halle-a-S.: Wilhelm Knapp. 1912. (3 M.).

THIS monograph gives a practical *résumé* of the manufacture of Epsom salts and magnesium chloride as by-

products of the potassium chloride and sulphate industry. The author has had extensive experience in chemical works for the manufacture of potash salts, and can give the young chemist who is at the beginning of his career valuable hints and practical advice. He has also made a thorough and careful study of the literature of the subject, and without overloading the monograph with references to other works, he points out where fuller information on various details is to be found. The potash industry has suffered comparative neglect in literature, and this addition to works on the subject will be cordially welcomed both in this country and in Germany.

*Die Chemischen Grundlehren nach Menge, Mass, und Zeit.* ("Chemical Fundamental Doctrines of Quantity, Mass, and Time"). By J. H. VAN'T HOFF. Braunschweig: Friedr. Vieweg und Sohn. 1912. (4 M.).

THIS book contains the text of a course of lectures on chemical theory delivered recently by Prof. van't Hoff. At the time of his death they were not quite ready for publication, but their editor, Prof. Ernst Cohen, has let them stand practically as they were, making as few alterations as possible in matters of detail and no additions whatever. The treatment of the subject follows very closely that adopted in the author's work, "Vorlesungen über Theoretische und Physikalische Chemie," and shows the same novelty in methods of attacking theoretical problems and the same incisive style in explanations. For students who have some knowledge of the elements of chemistry the book will be full of interest. It will undoubtedly put new ideas before them, widen their outlook, and show them fresh points of view.

*The Chemistry of the Rubber Industry.* By HAROLD E. POTTS, M.Sc. London: Constable and Co., Ltd. 1912.

THE author of this book has very skilfully steered his course between the Scylla of the over-elaboration of chemical information and the Charybdis of the exaggeration of the importance of purely utilitarian points of view, and has produced a book which both rubber technologists and chemists will find practically useful. He has been well advised to limit the number of references given in the text, merely giving at the end of each chapter some information as to the directions of further reading, and he shows a due sense of the value of space by not inserting unnecessary illustrations or photographs. The book opens with a chapter on colloidal chemistry in which modern views of the nature of the colloidal state and the general properties of colloids are very briefly discussed. The treatment of new rubber is next described, including its analysis and methods of mixing and the use of various compounding materials. Vulcanisation is fairly fully treated, some account being given of Dittmar's exhaustive study of the subject, and the analysis of vulcanised rubber is described and critically discussed.

*Julius Wilh. Brühl.* By K. AUWERS. Berlin: The German Chemical Society. 1912.

THIS pamphlet contains a lecture delivered by Prof. K. Auwers before the German Chemical Society in the memory of the late Julius Wilh. Brühl, and originally printed in the *Berichte* of the Society. The lecturer gave a short biographical sketch of the life of Prof. Brühl, showing how many and serious were the difficulties he had to contend with owing to his persistent ill health, and how striking was the contrast between the weakness of his body and the vigour and activity of his mind. His great scientific achievements were appreciatively outlined in the lecture, and an index of all his publications is given in the reprint.

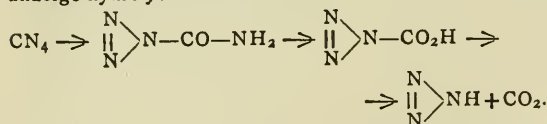
## CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperatures are Centigrade unless otherwise expressed.

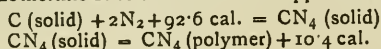
*Comptes Rendus Hebdomadaires des Séances de l'Académie des Sciences.* Vol. cliv., No. 19, May 6, 1912.

**Separation of Iron and Titanium.**—F. Bourion.—Mixtures of the oxides of iron and titanium can be analysed by chlorinating them with a mixture of hydrochloric acid gas and  $\text{S}_2\text{Cl}_2$ . If the quantity of sulphur chloride is small the oxide of iron is transformed into volatile chloride and the titanic acid is not attacked. The temperature must not exceed  $700-750^\circ$ , and the current of gases must not pass at a greater rate than 40 bubbles per minute at this temperature. The richer the mixture is in iron the longer the experiment takes. On cooling, the weight of the titanic acid is determined by weighing the boat containing the mixed oxides, and the iron is precipitated in the liquid through which the current of gases passed. Hydrochloric acid gas can be used alone, but the reaction is much slower.

**Carbon Pernitride.**—G. Darzens.—A pernitride of carbon,  $\text{CN}_4$ , can be prepared as follows:—5.3 grms. of pure freshly prepared cyanogen bromide are added in portions to a cooled solution of 3.25 grms. of sodium hydrazoate in 15 grms. of water. The bromide dissolves, and a little heat is generated. After some hours the liquid becomes homogeneous. It is treated with ether, and the ethereal solution is evaporated in a current of dry air at the ordinary temperature. The pernitride then remains behind as a colourless liquid which readily crystallises. The equation is  $\text{N}_3\text{Na} + \text{BrCN} = \text{NaBr} + \text{N}_3\text{C}\equiv\text{N}$ . Thus prepared, carbon pernitride is a colourless crystalline body, odourless, and melting at  $35.5-36^\circ$ . It is soluble in water, alcohol, ether, and most organic solvents. At temperatures below its melting-point it can be sublimed *in vacuo*. At  $70^\circ$  it begins to decompose, and between  $170^\circ$  and  $180^\circ$  it explodes with violence. It is very sensitive to blows, and should be prepared in small quantities only. When quite pure it can be kept for some time, but in presence of traces of bromine it yields a polymer, insoluble in ether, which, like paracyanogen, is more stable than the original substance. Aqueous solutions of the pernitride readily undergo hydrolysis as follows:—



With great difficulty determinations of the heat of formation were performed, and it was found that it is the most endothermic substance known. Approximately,—



**Zirconium Oxychlorides.**—Ed. Chauvenet.—Zirconium yields two series of oxychloride compounds. The first are the hydrates of zirconyl chloride,  $\text{ZrOCl}_2$ , which apparently does not exist in the anhydrous state. The author has obtained the following members of this series:— $\text{ZrOCl}_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{ZrOCl}_2 \cdot 3.5\text{H}_2\text{O}$ ,  $\text{ZrOCl}_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ . The other oxychlorides are hydrates of the complex oxychloride,  $\text{ZrOCl}_2 \cdot \text{ZrO}_2$ , viz.,  $\text{ZrOCl}_2 \cdot \text{ZrO}_2$ ,  $\text{ZrOCl}_2 \cdot \text{ZrO}_2 \cdot \text{H}_2\text{O}$ ,  $\text{ZrOCl}_2 \cdot \text{ZrO}_2 \cdot 3\text{H}_2\text{O}$ . The oxychloride,  $\text{ZrOCl}_2 \cdot \text{ZrO}_2$ , is decomposed by the action of heat into volatile  $\text{ZrCl}_4$  and  $\text{ZrO}_2$ .

**Preparation of  $\alpha\beta$ -Diketonic Ethers.**—A. Wahl and M. Doll.—Nitrous vapours convert malonic ethers into mesoxalic ethers, and acetyl, propionyl, butyryl, and heptylacetic ethers into  $\alpha\beta$ -diketonic ethers. Thus this reaction appears to be a general method of oxidising a

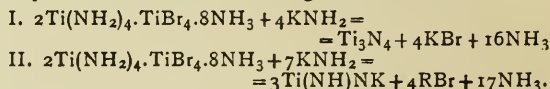
$\text{CH}_2$  group of an aliphatic compound to a carbonyl group. The  $\alpha\beta$ -diketonic ethers, e.g., ethyl propionylglyoxylate,  $\text{CH}_3\text{CH}_2\text{CO.CO.COOC}_2\text{H}_5$ , are yellow mobile liquids of agreeable odour. They boil without decomposition *in vacuo* at a temperature not far from the boiling-point of the original  $\beta$ -ketonic ether.

**Decomposition of Glycerin by Ultra-violet Rays.**—Victor Henri and Albert Ranc.—When subjected to the action of the ultra-violet rays emitted by a very powerful quartz lamp, the molecule of glycerin is rapidly broken down, the products being formic aldehyde, acids, and other substances containing an aldehyde group. Hydrogen peroxide accelerates this degradation.

*Berichte der Deutschen Chemischen Gesellschaft,*  
Vol. xlv., No. 7, 1912.

**Mirror Image Isomerism of Rhodium Compounds.** A. Werner.—Triethylene-diamine rhodium salts can be obtained by the action of ethylene diamine monohydrate on sodium rhodium sesquichloride. They are quite colourless, and usually crystallise in glassy well-formed crystals. When the chloride is precipitated with sodium camphor nitronate a difficultly soluble camphor nitronate is obtained, which is the laevo salt, while the more soluble salt of the *d*-series remains in the liquid. The isomers can also be separated by the addition of silver tartrate. The active compounds are very stable, and their aqueous solutions can be evaporated without affecting their rotatory power. The rotatory power of the rhodium compounds is the opposite of that of the cobalt and chromium compounds.

**New Titanium Compounds.**—Otto Ruff and Oskar Treidel.—The ammonium compound of titanium tetrabromide,  $\text{TiBr}_4 \cdot 8\text{NH}_3$ , when washed with liquid ammonia yields an orange coloured bromide of an amido-titanium nitride; its composition varies, according to the duration of washing, but always within the limits of the formulæ  $2\text{Ti}(\text{NH}_2)_4 \cdot \text{TiBr}_4 \cdot 8\text{NH}_3$  and  $3\text{Ti}(\text{NH})_2 \cdot \text{TiBr}_4 \cdot 8\text{NH}_3$ . When this compound is treated with an equivalent quantity of potassium amide the following reactions occur:—



The new titanium nitride,  $\text{Ti}_3\text{N}_4$ , obtained in the first reaction, is decomposed by water, giving titanium oxide hydrate and ammonia. It is brown in colour, thus differing from the blue-black nitride already known. When heated it decomposes as follows:— $\text{Ti}_3\text{N}_4 = 3\text{TiN} + \text{N}$ . Titanium diimide potassium,  $\text{Ti}(\text{NH})\text{NK}$ , is a brown-red salt which is readily decomposed in air, giving a greenish residue of potassium titanate and potassium oxide. It reacts energetically with water.

## NOTES AND QUERIES.

\*. Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertisement columns.

**Sea-water in Rivers.**—What is the simplest and at the same time reliable test for the presence (in minute quantities) of sea-water in the lower reaches of rivers? Is there any recognised method of estimating (without experiment) the highest point to which sea-water goes up a river at "spring tides," given the highest point to which the tide rises in that river?—W. D.

## MEETINGS FOR THE WEEK.

MONDAY, July 1st.—Royal Institution, 5. General Meeting.  
TUESDAY, 2nd.—Faraday Society, 8. (Annual General Meeting).  
"Electrocapillary Pulsation of a Mercury Meniscus," by A. P. Rosdestwensky and W. C. McC. Lewis.  
"Variation of the Conductivity of Aluminium Anode Films with Temperature," by G. E. Baird.



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